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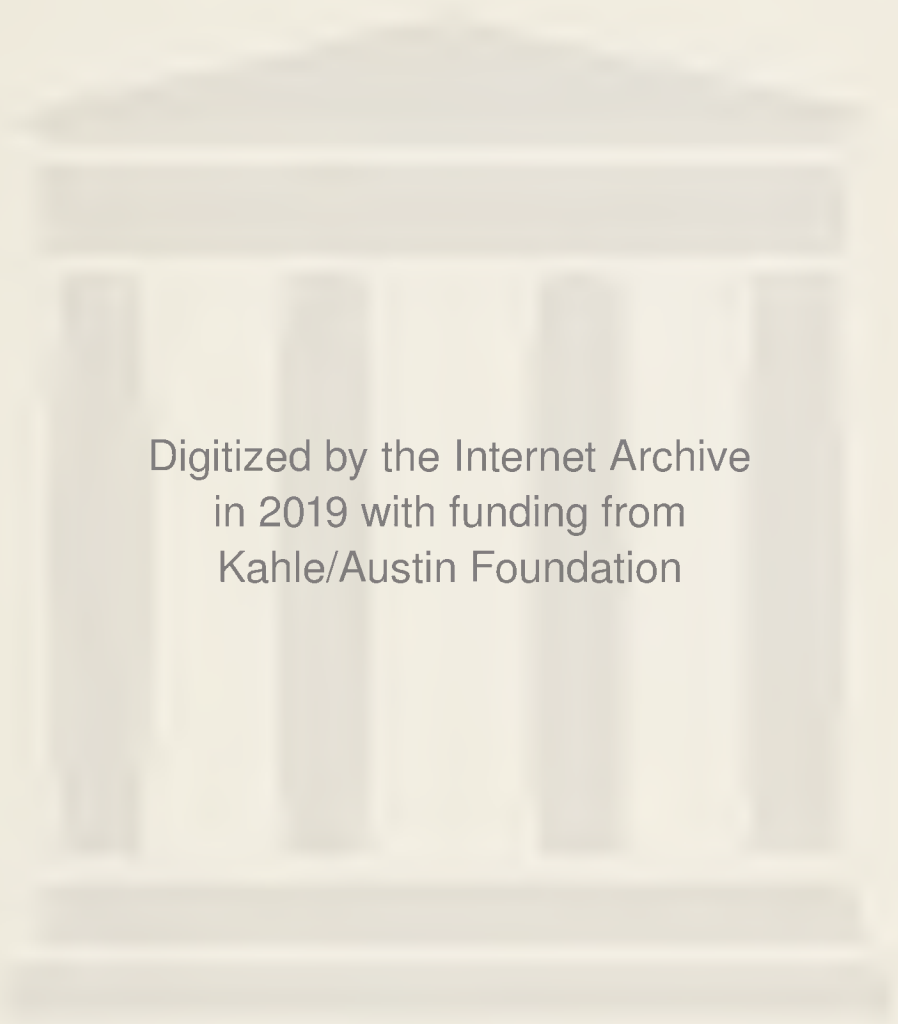
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ADVANCES IN CHEMICAL PHYSICS

VOLUME XI

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ADVANCES IN CHEMICAL PHYSICS

Edited by I. PRIGOGINE
University of Brussels, Brussels, Belgium

VOLUME XI

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INTRODUCTION

In the last decades, chemical physics has attracted an ever-increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity

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has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

CONTRIBUTORS TO VOLUME XI

A. R. Allnatt, Department of Chemistry, University of Manchester, Manchester, England

A. Bellemans, Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

Milton Blander, North American Aviation Science Center, Thousand Oaks, California, U.S.A.

J. Brocas, Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

N. Hasselle-Schuermans, Université Libre de Bruxelles, Brussels, Belgium

V. Mathot, Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

J. Philippot, Université Libre de Bruxelles, Brussels, Belgium

P. Résibois, Université Libre de Bruxelles, Brussels, Belgium

M. Simon, Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium

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PART I

EQUILIBRIUM STATISTICAL MECHANICS

STATISTICAL MECHANICS OF POINT-DEFECT INTERACTIONS IN SOLIDS

A. R. ALLNATT, *Department of Chemistry, University of Manchester, Manchester, England*

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I. INTRODUCTION

This article is concerned with the statistical mechanics of interactions between point defects in solids at thermodynamic equilibrium. The review is made entirely from the point of view of the

cluster formalism recently presented.[3,4] Although cluster methods are very familiar in the theory of classical gases and dense fluids they have had hardly any impact on the statistical mechanics of defects. This seems a pity because the formalism allows a very concise development and also allows one to take full advantage of certain developments in the theory of fluids.

The remainder of Section I is devoted to a rather brief review of earlier work in the field in order to gain a little perspective. In Sections II to IV the basic results of the cluster method are derived. In Section V a very brief account of the application of the formal equations to some systems with short-range forces is given. Section VI is devoted to a review of the application to systems with Coulomb forces between defects, where the cluster formalism is particularly advantageous for bringing the discussion to the level of modern ionic-solution theory.[25] Finally, in Section VII a brief account is given of Mayer's formalism for lattice defects[59] since it is in certain respects complementary to that principally discussed here. We would like to emphasize that the material in Sections V and VI is illustrative of the method. This is not meant to be an exhaustive review of results obtainable.

The notion of point defects in an otherwise perfect crystal dates from the classical papers by Frenkel[22] and by Schottky and Wagner.[75,85] The perfect lattice is thermodynamically unstable with respect to a lattice in which a certain number of atoms are removed from normal lattice sites to the surface (vacancy disorder) or in which a certain number of atoms are transferred from the surface to interstitial positions inside the crystal (interstitial disorder). These forms of disorder can occur in many elemental solids and compounds. The formation of equal numbers of vacant lattice sites in both M and X sublattices of a compound M_aX_b is called Schottky disorder. In compounds in which M and X occupy different sublattices in the perfect crystal there is also the possibility of antistructure disorder in which small numbers of M and X atoms are interchanged. These three sorts of disorder can be combined to give three hybrid types of disorder in crystalline compounds. The most important of these is Frenkel disorder, in which equal numbers of vacancies and interstitials of the same kind of atom are formed in a compound. The possibility of Schottky–antistructure disorder (in which a vacancy is formed by

transferring an atom from its own sublattice to an additional site on a "wrong" sublattice) and of interstitial–antistructure disorder (involving interstitial atoms of one sort and misplaced atoms of the other sort) was pointed out much later by Kröger,[42] but so far only the former has been observed.[41] In actual systems the types of disorder described may occur simultaneously. For example, it has been suggested that both Schottky and cationic Frenkel disorder occur in silver bromide.[41] The units which make up the various types of disorder, namely interstitial atoms, misplaced atoms, vacant lattice sites, are referred to as point defects. It is also convenient to include impurity atoms under this term.

The papers of Wagner and Schottky contained the first statistical treatment of defect-containing crystals. The point defects were assumed to form an "ideal solution" in the sense that they are supposed not to interact with each other. The equilibrium number of intrinsic point defects was found by minimizing the Gibbs free energy with respect to the numbers of defects at constant pressure, temperature, and chemical composition. The equilibrium between the crystal of a binary compound and its components was recognized to be a statistical one instead of being uniquely fixed.

One of the first detailed applications of these ideas was to the interpretation of ionic conductivity in simple ionic crystals. The vacancies in strongly ionic solids (e.g. alkali halides, silver halides, alkaline earth oxides) are ionic vacancies, i.e. they carry effective electrical charges equal and opposite to those of the missing ions. Similarly, an interstitial ion has an effective charge equal to the charge on the ion. Since the bulk of the crystal is electrically neutral it follows that in a pure uni-univalent stoichiometric crystal the numbers of oppositely charged defects must be equal. Since antistructure disorder is clearly unlikely, either Schottky or Frenkel disorder, or both, are the most probable forms of disorder in an ionic crystal, and ionic conduction can occur through the migration of the defects. An important method of distinguishing between the two possibilities and also of finding the number and mobility of the defects was devised by Koch and Wagner[39] and makes use of conductivity measurements on both the pure crystal and crystals containing small, controlled amounts of divalent

cations. Provided these impurities are incorporated substitutionally in the crystal a vacancy must be added for every impurity ion to maintain electrical neutrality, and hence the number of additional vacancies is known. In this way alkali halide crystals have been shown to contain Schottky defects and AgBr and AgCl predominantly cationic Frenkel defects. More recently, the dynamics of the defects has been studied by a wide variety of techniques including dielectric loss,[50] nuclear magnetic resonance,[72] and paramagnetic resonance.[86] Recent work, principally diffusion and conductivity studies, has been reviewed by Lidiard.[53] The defects also make contributions to the equilibrium thermodynamic properties, but for ionic crystals these contributions are so small that it is only in relatively recent years that these contributions have been measured in favourable cases (e.g. the specific heat,[15] thermal expansion,[88] and adiabatic compressibility[82] of silver bromide. In this substance the site fraction of cation vacancies may be as high as 10^{-2} at the melting point. The degree of disorder appears to be smaller than this for most simple ionic solids, e.g. approximately 10^{-4} for sodium chloride at the melting point).

Since ionic vacancies are electrically charged they may trap electrons or holes into localized states. For example, KCl which has been heated in potassium vapour contains an excess of anion vacancies and these trap the electrons from the potassium ions to give *F*-centres. In the period following the Schottky–Wagner papers extensive studies of the formation and properties of such colour centres were commenced (see e.g. Mott and Gurney[66]). The Schottky–Wagner ideas also gave a background for the consideration of nonstoichiometry in a wide range of other solids. For example, $Fe_{1-x}O$ and $Fe_{1-x}S$ were found to contain cation vacancies but apparently perfect anion sublattices.[38] Studies were also made of titanium oxides and chalcogenides, the palladium hydride system, and various transition metal oxides and sulphides and selenides. More recently, extensive studies of point defects have been made in other materials, particularly metals[46] and semiconductors,[74] by diffusion studies and many other techniques.

The observations on defect-containing crystals show that they fall broadly into two groups. In the first group the deviations from

the perfect crystal structure are detectable but very small. Examples are the intrinsic lattice disorder occurring in metals, in simple ionic conducting solids such as NaCl, AgBr noted above, and in ionic semiconductors such as PbS_{1-x}, ZnO_{1-x}, and F-centres in alkali halides. The second group comprises compounds which show gross deviations from stoichiometry, e.g. $Fe_{0.84}O$, the palladium hydride system, and very many other hydrides, oxides, and chalcogenides of transition metals. Anderson[7] has recently reviewed some of the characteristics of this group (see also the other papers in this book), in which a high proportion of the defects must be adjacent to each other or in small clusters of defects. The systems we have in mind in the present discussion belong primarily to the first group. However in Section VII we review briefly a method which should prove valuable for systems with larger deviations from stoichiometry, although detailed calculations are so far lacking.

Results of the "ideal solution" approach were found to be identical with those arrived at on the basis of a simple quasi-chemical method. Each defect and the various species occupying normal lattice positions may be considered as a separate species to which is assigned a "chemical potential", $\bar{\mu}$, and at equilibrium these are related through a set of stoichiometric equations corresponding to the "chemical reactions" which form the defects. For example, for Frenkel disorder the equation will be

$$\bar{\mu}_i + \bar{\mu}_v = \bar{\mu}_l \tag{1}$$

corresponding to the reaction:

$$\begin{matrix}\text{Interstitial} \\ \text{atom}\end{matrix} + \begin{matrix}\text{Vacant lattice} \\ \text{site}\end{matrix} = \begin{matrix}\text{Atom in normal} \\ \text{lattice site}\end{matrix}$$

The quantities $\bar{\mu}$ are not Gibbs chemical potentials since their definition involves the defect composition of the crystal. We shall call them defect chemical potentials and they are defined by the relation

$$\bar{\mu}_s = \left(\frac{\partial G}{\partial N_s}\right)_{T,P,N_r \neq N_s} \tag{2}$$

where G is the Gibbs free energy of the crystal. From the "ideal solution" expression for G the chemical potentials are quickly

found; for a small degree of Frenkel disorder we have

$$\begin{aligned} \bar{\mu}_i &= g_i + kT \log c_i + \mu_l^0 \\ \bar{\mu}_v &= g_v + kT \log c_v \\ \bar{\mu}_l &\simeq \mu_l^0 \end{aligned} \tag{3}$$

and Eq. (1) yields at once

$$c_i c_v = K = \exp\left[-(g_i + g_v)/kT\right] \tag{4}$$

In these equations g_v is the change in Gibbs free energy on taking one atom from a normal lattice site to the surface of the crystal and $(g_i + g_v)$ the change when an atom is taken from a normal lattice site to an interstitial site, both at constant temperature and pressure. c_r denotes a site fraction of species r on its sublattice, and μ_l^0 is the chemical potential of a normal lattice ion in the defect-free crystal.

The quasi-chemical method, namely the use of a set of reaction equations and corresponding equilibrium constants analogous to Eqs. (1) and (4), is the most widely used approach to defect properties and is presented in detail in the book by Kröger.[41] (We should note that there is a degree of arbitrariness in writing the reaction equations and defining a set of defect chemical potentials. This point is fully discussed by Kröger, sections 7.8 and 22.13. The definition above corresponds to assigning chemical potentials to what he calls "structure elements".) The corresponding defect chemical potentials are of value in discussions of matter transport via defects using the methods of irreversible thermodynamics.[6,37]

In the interpretation of many experiments, both equilibrium and non-equilibrium, it becomes necessary to recognize that defects interact so that their relative distribution is no longer random. For example, in the interpretation of thermal expansion measurements on aluminium[79] it is necessary to recognize the possibility of divacancies (two vacancies on adjacent lattice sites). The quasi-chemical method is then extended, the equilibrium between the species divacancy and vacancy being described by an additional mass-action equation and a certain binding energy, and the divacancy can be assigned a defect chemical potential as a separate species. Trivacancies or higher aggregates each characterized by further equilibria may exist. The quasi-chemical

method is thus quite simply extended to compound defects such as nearest-neighbour aggregates or vacancies trapped as neighbours to solute atoms. In ionic crystals where the defect interactions are Coulombic except at small separations, the interactions are of long range and relatively important in their effect on defect-controlled properties. The interactions of divalent cations and cation vacancies in a sodium-chloride-like crystal are of particular interest in connection with the Koch and Wagner type of experiment described above. The extension of the quasi-chemical method is somewhat less straightforward in this case. Lidiard[51] has treated the thermodynamics of such a system by distinguishing between neutral "complexes", composed of a vacancy and an impurity ion on adjacent sites and characterized by a binding energy, and the interactions among defects not involved in complexes. The contribution of the latter interactions to the total free energy of the system was calculated by applying the results of the Debye–Hückel theory of electrolyte solutions. The effect of these interactions on the equilibrium could then be found. The use of this sort of theory, which is essentially a modification of the Bjerrum[11] theory of electrolyte solutions, and its assumptions will be reviewed in detail in a later section (VI-A). We may note here however that the Debye–Hückel law is only a limiting one and is derived for the case of a continuum rather than for discrete lattice sites. Furthermore it is recognized that the concept of a "complex" appears to be slightly arbitrary when considered in detail. Although the method is presumably quite adequate at low enough concentrations it is difficult to pin down the conditions under which deviations become important or to develop within the same framework a theory valid at high concentrations. (This particular problem provided one of the strongest motivations for setting up the cluster formalism.)

The preceding paragraphs illustrate that analogies between point defects in a crystal and solute molecules in a solution have been used previously but in a fairly elementary way. However, the implications of the existence of such analogies in the formulation of the statistical mechanics of interacting defects has not been considered in detail apart from an early paper by Mayer,[59] who was interested primarily in the relation of defect interactions to the solid–liquid phase transition in crystals with short-range forces. The

formalism described here is analogous in intent to the McMillan–Mayer[64,33] theory of solutions and is suitable for crystals containing small concentrations of defects, up to say one per cent. The contribution of the defect interactions to each thermodynamic function can be expressed as a "cluster expansion", i.e. a power series in the concentration of the defects. The coefficients of the power series are defined in terms of the summations over coordinates of functions analogous to the "f" functions of imperfect gas and solution theory.[33] In particular, the expressions for the defect chemical potentials and the expressions for defect concentrations derived from them are merely changed by the inclusion of activity coefficients for which cluster expansions are available. The use of the law of mass action is thus avoided. Within such a formalism the spatial distribution of defects, previously described in terms of "complexes", divacancies, or higher aggregates using the law of mass action, must be reformulated as the study of the relative distribution functions of the defects. Cluster expansions are derived for these quantities. These quantities prove essential for a systematic development of the phenomenological coefficients in diffusion,[26] although we shall not discuss this here.

II. CONFIGURATIONAL SPECIFICATION OF DEFECT-CONTAINING CRYSTALS

To state clearly the problem at hand it is necessary to introduce initially a detailed notation for the composition of a crystal. For much of the later manipulations it is possible to use a very much simpler, abbreviated version of the notation. From the point of view of thermodynamics, the composition of an imperfect crystal is specified when the number of atoms of each of the different chemical species present is given. Let atoms which appear in a perfect crystal be denoted by a subscript 0, and let $\mathbf{N}_0$ denote the N_0 atoms of σ different species $(N_{01}, N_{02}, \ldots, N_{0\sigma})$, all of which species appear in the perfect crystal, i.e.

$$\mathbf{N}_0 = \sum_{s=1}^{\sigma} N_{0s} \tag{5}$$

Let $\mathbf{N}_a$ denote the set of N_a atoms of ν species $(N_{a1}, N_{a2}, \ldots, N_{a\nu})$,

none of which species occurs in a perfect crystal of the material, so that

$$\mathbf{N}_a = \sum_{s=1}^{\nu} N_{as} \tag{6}$$

Then the composition of an imperfect crystal is given thermodynamically by the set of numbers $\mathbf{N} = \mathbf{N}_0 + \mathbf{N}_a$. For each species there is a chemical potential; thus μ_{0s} is the chemical potential for an atom of species $0s$, $\boldsymbol{\mu}_0$ denotes the set of σ such quantities, and similarly for $\boldsymbol{\mu}_a$.

We turn now to the microscopic description of an imperfect crystal. The various defects in any imperfect crystal can be imagined to be formed from a corresponding perfect crystal by one or more of the following processes: (a) remove an atom of species $0s$ from the crystal leaving a vacant lattice site, (b) remove an atom of species $0s$ from the crystal and replace it by an atom of a different species (either $0t$ or at), (c) add to the crystal an atom of any species to a site on a sublattice unoccupied in the perfect crystal. We refer to the latter as atoms in interstitial positions. Let $\mathbf{B}$ be a set of numbers such that B^r is the number of sites on sublattice number r in the perfect crystal, and let ϕ be the number of sublattices in the crystal (including interstitial sublattices not occupied in the perfect crystal). The total number of sites of all kinds in the perfect crystal is then

$$B = \sum_{r=1}^{\phi} B^r \tag{7}$$

Thus atoms of species $0s$ may be found in an imperfect crystal in their normal lattice positions, occupying sites on the "wrong" sublattice (that is a sublattice occupied by an atom of a different species in the perfect crystal), or in interstitial positions. Let the numbers of such atoms be N_{0s}^R, N_{0s}^W, N_{0s}^I, respectively, so that

$$N_{0s} = N_{0s}^R + N_{0s}^W + N_{0s}^I \tag{8}$$

An atom on a wrong sublattice may be classified according to the number of the sublattice it is on (and hence the species of atom it has replaced). Thus, we have

$$N_{0s}^W = \sum_{r=1}^{\theta}{}' N_{0s}^{Wr} \tag{9}$$

where N_{0s}^{Wr} is the number of atoms of species $0s$ which occupy sites on sublattice number r, which would be occupied by some other species $0t$ in the perfect crystal. In Eq. (9), the limit of the summation, θ, is the number of occupied sublattices in the perfect crystal. The prime indicates the exclusion from the sum of sublattices occupied by atoms of species $0s$ in the perfect crystal. In a similar manner if N_{0s}^{Ir} is the number of interstitial atoms of species $0s$ which occupy interstitial sites of kind r, then

$$N_{0s}^{I} = \sum_{r=1}^{\tau} N_{0s}^{Ir} \tag{10}$$

where τ is the number of kinds of interstitial sites. Similarly we have

$$N_{0s}^{R} = \sum_{r=1}^{\theta}{}' N_{0s}^{Rr} \tag{11}$$

where N_{0s}^{Rr} is the number of species $0s$ on "right" lattice sites of type r. Here the prime indicates the exclusion of sublattices occupied by atoms of species $0t \neq 0s$ in the perfect crystal. The N_{as} solute atoms of species as may occupy interstitial or substitutional positions. If the numbers of such atoms are N_{as}^{I}, N_{as}^{S} respectively then

$$N_{as} = N_{as}^{I} + N_{as}^{S} \tag{12}$$

$$N_{as}^{I} = \sum_{r=1}^{\tau} N_{as}^{Ir} \tag{13}$$

$$N_{as}^{S} = \sum_{r=1}^{\theta} N_{as}^{Sr} \tag{14}$$

where N_{as}^{Ir} is the number of solute atoms of type as which occupy interstitial sites of type r, and N_{as}^{Sr} is the number of solute atoms of the same kind which are substitutionally incorporated into the crystal replacing an atom on sublattice number r. In addition to sites occupied in the various ways already described there may be vacant lattice sites. Let N_{0s}^{Vr} be the number of vacant lattice sites on sublattice number r which have been formed by removing an atom of type $0s$ from the perfect crystal.

A notation for the various sets of atoms defined in the last paragraph will now be introduced. Let $\mathbf{N}_0^W$ denote the set of

numbers (N_{01}^{W2}, N_{01}^{W3}, . . .), a typical member of the set being N_{0s}^{Wr}. Similarly, let $\mathbf{N}_0^R$, $\mathbf{N}_0^I$, $\mathbf{N}_a^S$, $\mathbf{N}_a^I$, $\mathbf{N}_0^V$ denote the sets of numbers, typical members of which sets are N_{0s}^{Rr}, N_{0s}^{Ir}, N_{as}^{Sr}, N_{as}^{Ir}, N_{0s}^{Vr} respectively. The six sets of numbers just defined specify the microscopic composition of the lattice completely; their definitions and interrelations are summarized in Fig. 1. It should be

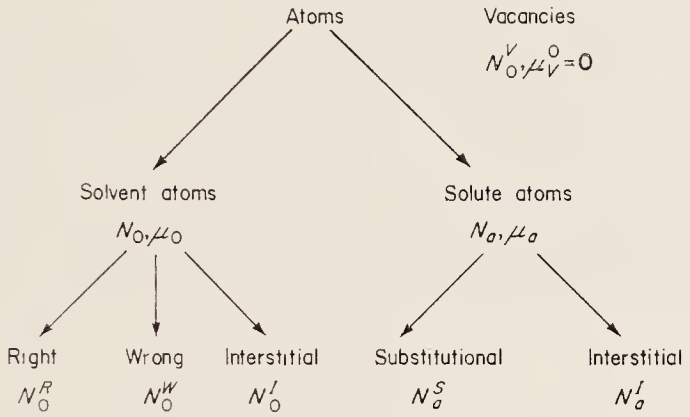

Fig. 1. Summary of the classification of atoms in an imperfect crystal.

noted that it is not necessary to specify the chemical potential of a species in such detail because for a system in equilibrium the chemical potential of a species is the same whatever the site it is occupying. The chemical potential of a vacancy is zero because it is a structural rather than a compositional entity; making a vacancy need not involve transfer of the atom to a reservoir.

Having clearly stated in detail the microscopic composition, we now introduce a simpler, abbreviated notation which is convenient for the subsequent manipulations. The set of numbers $\mathbf{N}_0^R$ may be relabelled to give in their place a set of numbers $\mathbf{N}_1$, a typical member of the set being N_{1s}^r, which is the number of atoms of kind s on sublattice number r. The other five sets of numbers, $\mathbf{N}_0^W$, $\mathbf{N}_0^I$, $\mathbf{N}_a^S$, $\mathbf{N}_a^I$, $\mathbf{N}_0^V$, which specify completely the defect composition of the crystal, will be similarly relabelled to give a set of numbers $\mathbf{N}_2$, a typical member of the set being N_{2s}^r. The number N_{2s}^r is the number of defects of type s, and they are situated on the sublattice number r. (By the definitions employed, one kind of defect can only appear on one sublattice but one sublattice may contain more than one kind of defect. Although r is specified by s,

the double labelling of r and s in N_{2s}^r is used because it is convenient to be able to distinguish whether two different kinds of defect occupy the same or different sublattices.) The total number of defects on sublattice r is

$$N_2^r = \sum_{s_r=1}^{\gamma(r)} N_{2s}^r \tag{15}$$

where $\gamma(r)$ is the number of different sorts of defect on sublattice number r. The sum is over the $\gamma(r)$ types of defect s_r on the r sublattice. The microscopic composition of the crystal is completely specified by the set of numbers $(\mathbf{N}_1 + \mathbf{N}_2)$, and $\mathbf{N}_2$ refers solely to the defect composition.

It is convenient to employ the set notation of Meeron[61] with minor modifications suited to the present problem. Thus for a set of defects $\mathbf{N}_2$ of ω kinds we define

$$\mathbf{N}_2! = \prod_{s=1}^{\omega} N_{2s}^r! \tag{16}$$

and for a set of quantities $\mathbf{x}_2$ pertaining to the same set of particles

$$\mathbf{x}_2^{\mathbf{N}_2} = \prod_{s=1}^{\omega} (x_{2s}^r)^{N_{2s}^r} \tag{17}$$

We shall also employ the convenient notation

$$\mathbf{N}_2 \cdot \mathbf{x}_2 = \sum_{s=1}^{\omega} N_{2s}^r x_{2s}^r \tag{18}$$

For a crystal of ϕ sublattices we define

$$(\mathbf{N}_2!)^* = \prod_{r=1}^{\phi} N_2^r! \tag{19}$$

where N_2^r is defined by Eq. (15). Similarly we use the notation

$$(\mathbf{B}^{\mathbf{N}_2})^* = \prod_{r=1}^{\phi} (B^r)^{N_2^r} \tag{20}$$

We use the symbol $\{\mathbf{N}_2\}$ to denote a configuration of $\mathbf{N}_2$ defects, that is a particular assignment of the set of $\mathbf{N}_2$ defects, all distinguishable, to the lattice sites of the crystal, the latter being all labelled and distinguishable. Although the notation above is rather different from that generally employed in discussions of

defects it will be found to have great advantages in developing the statistical mechanics.

After these preliminaries we can now set up the partition function for a canonical ensemble of systems of composition $\mathbf{N} = \mathbf{N}_0 + \mathbf{N}_a$ in volume V at temperature T. It is

$$Q(\mathbf{N}, V, T, \mathbf{N}_2) = \sum_{\{\mathbf{N}_2\}} \sum_i \exp\left[-E_i(\mathbf{N}, V, \{\mathbf{N}_2\})/kT\right]/\mathbf{N}_2! \quad (21)$$

In the equation $E_i(\mathbf{N}, V, \{\mathbf{N}_2\})$ is one (number i) of a complete set of energy eigenvalues for a crystal of composition $\mathbf{N}$ and volume V in which $\mathbf{N}_2$ defects are in a specified configuration denoted by $\{\mathbf{N}_2\}$. (Implicit in this labelling of quantum states is the assumption that the kinetic energy associated with defect diffusion is negligible, as discussed below.) The summations are over all the eigenstates for a given configuration of defects and over all possible configurations of defects for the given composition and defect constitution $\mathbf{N}_2$. The factor $\mathbf{N}_2!$ arises because in specifying the configuration of defects we have treated defects of the same kind as distinguishable. The justification for the preceding equation may be found by considering briefly the application of the Born–Oppenheimer approximation to the crystal.

The Schrödinger equation for the system is

$$[T_N + T_E + V(\mathbf{r}, \mathbf{R})]\Psi(\mathbf{r}, \mathbf{R}) = E\Psi(\mathbf{r}, \mathbf{R}) \quad (22)$$

Here T_N and T_E are the kinetic energy operators for the nuclei and electrons respectively, and $V(\mathbf{r}, \mathbf{R})$ is the total Coulombic energy of nuclei and electrons. $\mathbf{r}$ and $\mathbf{R}$ denote the sets of coordinates of the electrons and nuclei respectively. One seeks wave functions of the form

$$\Psi(\mathbf{r}, \mathbf{R}) = \Phi(\mathbf{R}, \mathbf{r})\chi(\mathbf{R}) \quad (23)$$

The function Φ is determined approximately for a fixed set of $\mathbf{R}$ from the equation

$$[T_E + V(\mathbf{r}, \mathbf{R})]\Phi = U(\mathbf{R})\Phi \quad (24)$$

The eigenvalues of this equation have local minima, each one for some particular value of the coordinates $\mathbf{R}_0$, and U may be expanded about its value at the local minimum

$$U(\mathbf{R}) = U_0 + (\mathbf{R} - \mathbf{R}_0) \cdot \nabla U_0 + \tfrac{1}{2}[(\mathbf{R} - \mathbf{R}_0) \cdot \nabla]^2 U_0 + \ldots \tag{25}$$

The value of U for each local minimum is used to set up an equation for the nuclear motion

$$[T_N + U]\chi = E\chi \tag{26}$$

which determines the function $\chi(\mathbf{R})$ and a set of eigenvalues E_i. Equation (26) can be deduced by substitution of Eq. (23) in Eq. (22) neglecting the terms

$$\chi T_N \Phi + \sum_a \mathbf{p}_a \chi \cdot \mathbf{p}_a \Phi / 2m_a \tag{27}$$

and then multiplying by Φ^* and integrating over the electron coordinates. In Eq. (27) $\mathbf{p}_a$ is the momentum operator for nucleus a whose mass is m_a. Under the conditions that the Born–Oppenheimer approximation converges, the neglected terms can be treated as a small perturbation. Even if the convergence is poor, the classifying of states by means of local minima in U plus index i remains. If we neglect the contribution of diffusive motion to the energy of the system then the eigenenergy E_i is accurately the total energy of the system and is indeed a function of the configuration of the defects $\{\mathbf{N}_2\}$ (which is equivalent to the set of minimal positions $\mathbf{R}_0$) in the crystal of given composition and volume in the manner indicated in Eq. (21). Furthermore, the sum over states is the sum over the complete set of eigenvalues for a given configuration $\{\mathbf{N}_2\}$ (that is, for a given local minimum in $U(\mathbf{R})$), followed by a sum over all configurations $\{\mathbf{N}_2\}$ (that is, a sum over all local minima $U(\mathbf{R})$ for a crystal of defect composition $\mathbf{N}_2$). The complete expression for the partition function would of course contain a summation over all defect compositions $\mathbf{N}_2$ consistent with the given $\mathbf{N}$, V, T. We have retained in Eq. (21) only the eigenstates corresponding to the value of $\mathbf{N}_2$ found by minimizing the Helmholtz free energy $-kT \log Q(\mathbf{N}, V, T)$ at constant $\mathbf{N}$, V, T with respect to the set $\mathbf{N}_2$. The summation over eigenstates for a given configuration appearing in Eq. (23) can be written as

$$\sum_i \exp[-E_i(\mathbf{N}, V, \{\mathbf{N}_2\})/kT] = \exp[-F(\mathbf{N}, V, T;\ \{\mathbf{N}_2\})/kT] \tag{28}$$

where $F(\mathbf{N}, V, T; \{\mathbf{N}_2\})$ is a Helmholtz free energy. The free energy may be written in the form

$$F(\mathbf{N}, V, T; \{\mathbf{N}_2\}) = F_0(\mathbf{N}) + F(\mathbf{N}_2:\mathbf{N}) + F(\{\mathbf{N}_2\}) \tag{29}$$

Here $F_0(\mathbf{N})$ is the Helmholtz free energy for the perfect crystal from which the imperfect crystal of composition $\mathbf{N}$ can be imagined formed in the manner described in the second paragraph of this section. $F(\mathbf{N}_2:\mathbf{N})$ is the part of the Helmholtz free energy of the crystal of composition $\mathbf{N}$ containing $\mathbf{N}_2$ defects which is independent of the configuration of the defects, but dependent on the defect composition. $F(\{\mathbf{N}_2\})$ is the configuration-dependent part of the free energy. (All three quantities on the right-hand side of Eq. (29) are of course functions of V and T.) The expression for the partition function can be written in the required form, using Eqs. (28) and (29), as the product

$$Q(\mathbf{N}, V, T; \{\mathbf{N}_2\}) = Q_0 Q_c \tag{30}$$

where Q_0 is independent of defect configuration, and Q_c depends on the configuration of the defects.

$$Q_0 = \exp\left[-\left(F_0(\mathbf{N}) + F(\mathbf{N}_2:\mathbf{N})\right)/kT\right] \tag{31}$$

$$Q_c = \sum_{\{\mathbf{N}_2\}}{}' \left(\exp\left[-F(\{\mathbf{N}_2\})/kT\right]\right)/\mathbf{N}_2! \tag{32}$$

The summation is over all possible configurations of the defects, each defect being allowed to occupy any site on its particular sublattice subject to the restriction indicated by the prime that no two defects can occupy the same site. It is convenient to refer to this condition as the excluded site property.

It will be assumed that the free energy of interaction can be expanded as a sum of component potentials

$$F(\{\mathbf{N}_2\}) = \sum_{i,j \subset \mathbf{N}_2} F_{ij}^{(2)}(\{i, j\}) + \sum_{i,j,k \subset \mathbf{N}_2} F_{ijk}^{(3)}(\{i, j, k\}) + \cdots F_{N_2}^{(N_2)}(\{\mathbf{N}_2\}) \tag{33}$$

The first sum is over all pairs i, j of the set $\mathbf{N}_2$, and similar definitions apply to higher terms. The retention of higher order than pair interactions is essential for the problem at hand, but the

cluster method is only of value if the terms decrease fairly rapidly in magnitude, $F^{(N_2)}$ being negligible for large N_2.

The defect interaction energies appearing in Eq. (33) are, for the purposes of the present article, assumed to be known either from theory or experiment. Certain other quantities appear in the final expressions for the thermodynamic functions and must therefore be known. The quantity defined by the relation

$$F^r_{0is} = \left(\frac{\partial F_0(\mathbf{N})}{\partial N^r_{is}}\right)_{T,V,N^t_{ju}\neq N^r_{is}} \quad (i = 1, 2) \tag{34}$$

is equal to the chemical potential (in the pure crystal) of the atom which would occupy in the perfect crystal the site occupied by species is on sublattice r in the imperfect crystal. (It is zero for interstitial defects since, by definition, these sites are unoccupied in the perfect crystal.) We also require the defect formation energies defined by the relation

$$F^r_{2s} = F^r_{02s} + \left(\frac{\partial F(\mathbf{N}_2:\mathbf{N})}{\partial N^r_{2s}}\right)_{T,V,N^t_{2u}\neq N^r_{2s}} \tag{35}$$

The second term on the right hand of this equation has a simple meaning for each defect. For example, for a vacancy it is the change in Helmholtz free energy on forming the vacancy by transporting an atom from the site to infinite distance from the crystal at constant temperature and volume apart from the contribution from defect interactions. For other defects it is the change in free energy under the same conditions when the atom (if any) which occupies the site in the perfect crystal is removed from the crystal and replaced by the defect atom. It would be logical to review at this point the calculation of the defect formation energies for systems with small concentrations of point defects. However, the recent review by Howard and Lidiard includes just such an account.[37] We shall merely note here that adequate calculations of three-defect or higher-order interactions have not so far been made for even the simplest solids nor are they available with any certainty from experiment, although they may sometimes be important as will be noted in examples below. A comprehensive account of the defect interaction energies from both experiment and theory can be found in Kröger's book.[41]

III. THE SELECTION OF A STATISTICAL FORMALISM

In the preceding section we have set up the canonical ensemble partition function (independent variables **N**, V, T). This is a necessary step whether one decides to use the canonical ensemble itself or some other ensemble such as the grand canonical ensemble ($\boldsymbol{\mu}$, V, T), the constant pressure canonical ensemble (**N**, P, T), the "generalized" ensemble of Hill[33] ($\boldsymbol{\mu}$, P, T), or some form of constant pressure ensemble like those described by Hill[34] in which either a system of the ensemble is open with respect to some but not all of the chemical components or the system is open with respect to all components but the total number of atoms is specified as constant for each system of the ensemble. We now consider briefly the selection of the most convenient formalism for the present problem.

Although the object of the present work is a formalism for the calculation of thermodynamic functions and distribution functions analogous to the McMillan–Mayer theory of solutions,[33,64] there are fundamental differences between the two problems which require the adoption of significantly different approaches. The solution theory was developed using the formalism of the grand canonical ensemble. It was rigorously shown that thermodynamic functions such as osmotic pressure and chemical potentials of the solutes can be expressed as virial expansions in terms of the concentrations of the solute molecules. The nth virial coefficient is an integral over the coordinates of n solute molecules of an integrand depending on the coordinates of n solute molecules, and defined as a certain sum of products of the functions

$$f(\mathbf{R}_{ij}) = \exp\left(-w(\mathbf{R}_{ij})/kT\right) - 1 \tag{36}$$

$w(\mathbf{R}_{ij})$ is the potential of average force of two solute molecules i and j at a distance $\mathbf{R}_{ij}$ apart in the limit of infinite dilution. Because of the choice of the state of infinite dilution[33] as reference state, the thermodynamic functions of the solute such as activity coefficients calculated by this theory refer to a solution of the same composition and temperature as the experimental solution but maintained under a pressure relative to the reference solution

(assumed to be at one atmosphere) equal to the osmotic pressure of the solution. (The reference solution and the solution in the theory would thus be in thermodynamic, or "osmotic", equilibrium if they were separated by a semipermeable membrane.) Only with this choice of reference state is the complete separation of solute and solvent properties achieved whereby the solvent properties enter only through the definition of the potential of average force to be used in Eq. (36). For example, in the case of an ionic solution, the potential of average force between two ions at large separation is taken to be the Coulomb interaction $z_i z_j e^2/R_{ij}D$, where z_i and z_j are the valences of the ions and D is the dielectric constant of the pure solvent. In the case of defects in an ionic solid such as silver bromide the use of such a reference state and the concept of osmotic equilibrium are not satisfactory. For, with the relatively high concentrations of defects encountered in such a solid it is important to note that such properties of the crystal as the dielectric constant and the average lattice parameter vary markedly with the number of defects. It would appear preferable to construct a formalism in which the properties of the imperfect crystal studied, such as dielectric constant, are employed, rather than to use a formalism which requires such parameters referring to a crystal in a hypothetical reference state which cannot be studied experimentally (e.g. a silver bromide crystal with no Frenkel defects). This restriction means that in practice we must select an ensemble in which all the systems have the same composition. For example, the grand canonical ensemble is unsuitable.

The majority of experiments in defect-containing solids are conducted at a known, constant pressure. In favourable cases they may yield values for the Gibbs free energy of interaction of the defects. One might hope that it would be possible to construct a theory based on the constant pressure canonical ensemble in which the interaction parameters appearing in the final cluster development are Gibbs free energies rather than the Helmholtz free energies which appear in the case of the canonical ensemble. In practice, we have not found it possible to carry out such a programme in a convincing manner, and we shall therefore restrict present work to the following procedure. The Helmholtz free energy is to be calculated according to the equation

$$F(\mathbf{N}, V, T) = -kT \log Q(\mathbf{N}, V, T)$$
$$= -kT \log Q(\mathbf{N}, V, T; \{\mathbf{N}_2\})_{\min.} \quad (37)$$

and is a function of volume. We consider an experimental crystal at a known pressure and temperature. The condition for equilibrium is that we minimize the Gibbs free energy:

$$\left[\frac{\partial}{\partial V}(F(\mathbf{N}, V, T) + PV)\right]_{\mathbf{N},T,P} = 0 \quad (38)$$

IV. CLUSTER EXPANSIONS

A. The Helmholtz Free Energy

We shall now obtain the virial expansion of the configuration-dependent part of the partition function Q_c defined in Eq. (32), analogous to the well-known virial expansion for a mixture of imperfect gases. Although the expansion could be obtained by modifying the method of Fuchs[26] to account for the complications introduced by restricting each defect to sites on its own sublattice and also the excluded site property, we shall use instead a very simple and elegant procedure first employed by Brout.[13] The same method also allows a simple and complete treatment to be given for the distribution functions, which would be difficult to deal with by other methods (see Section IV-C).

By taking the logarithms of both sides of Eq. (32) we have the equation

$$\log Q_c = \log Q_c^0 + \log Q_c^1 \quad (39)$$

Q_c^0 is the value of Q_c when the free energy of interaction between the $\mathbf{N}_2$ defects is zero,

$$Q_c^0 = (\mathbf{B}\,!)^*/([\mathbf{B} - \mathbf{N}_2]\,!)^*\mathbf{N}_2\,! \quad (40)$$

using the notation of Eqs. (16) and (19), and the remaining term is defined by

$$\log Q_c^1 = \log \{(\sum_{\{\mathbf{N}_2\}}{}' e^{\beta F})/(\mathbf{B}^{\mathbf{N}_2})^*\} \quad (41)$$

where $F \equiv F(\{\mathbf{N}_2\})$, $\beta = -1/kT$, and we have taken advantage of the fact that

$$(\mathbf{B}\,!)^*/([\mathbf{B} - \mathbf{N}_2]\,!)^* \to (\mathbf{B}^{\mathbf{N}_2})^*$$

for large B^r. We consider first the evaluation of Eq. (41).

In order to make the linked cluster expansion it is necessary to remove the excluded-site restriction on the summation by writing

$$\log Q_c^1 = \log \{(\sum_{\{\mathbf{N}_2\}} [e^{\beta F} \prod_{r=1}^{\phi} \prod_{i,j \subset N_2{}^r} (1 + h_{ij})])/(\mathbf{B}^{\mathbf{N}_2})^*\}$$
$$= \log \langle e^{\beta F} \rangle_{\mathbf{N}_2} \tag{42}$$

The summation is here over all possible configurations of the defects on the lattice, each defect being able to occupy any site on its particular sublattice. Configurations in which more than one defect is assigned to a particular lattice site are now included in the summation, but such configurations do not contribute to the partition function because of the definition of the functions h_{ij},

$$h_{ij} = -\delta_{ij} \tag{43}$$

where δ_{ij} is the Kroenecker delta function. Thus h_{ij} is -1 when defects i and j occupy the same site and is zero for all other configurations. The value of F when two defects i and j occupy the same site is arbitrary. It is convenient to take

$$F_{ij}^{(2)} = F_{ijk}^{(3)} = \ldots = 0, \text{ for } i = j. \tag{44}$$

Equation (42) also defines the angular brackets to indicate the process of averaging in the manner just described over the configurations of $\mathbf{N}_2$ defects.

We can now make the semi-invariant expansion of Eq. (42). The nth semi-invariant M_n is defined by the relation

$$\log \langle e^{\beta x} \rangle = \sum_{n=1}^{\infty} M_n \beta^n / n! \tag{45}$$

where x is a random variable and the brackets denote an average over x according to a known distribution law. The M_n are the Thiele semi-invariants in the theory of statistics,[17] the first two being

$$M_1 = \langle x \rangle \tag{46}$$

$$M_2 = \langle x^2 \rangle - \langle x \rangle^2 \tag{47}$$

The use of the semi-invariant expansion depends on the observation that if x_1 and x_2 are independent random variables for which

exist semi-invariants $M_n(x_1)$ and $M_n(x_2)$, then from Eq. (45)

$$M_n(x_1 + x_2) = M_n(x_1) + M_n(x_2) \tag{48}$$

Therefore in the semi-invariant expansion of two independent variables there appear no cross terms in any semi-invariant $M_n(x_1 + x_2)$. The result is easily generalized to n independent variables.

In Eq. (42) F may be considered as a random variable in the coordinates of the $\mathbf{N}_2$ defects. The distribution law is that every defect can take up any one of the sites on its sublattice with equal probability and independently of the positions of the other defects. The correlation between the positions of the defects implied by the original distribution law in Eq. (41) has been removed by introducing the h functions.

The semi-invariant expansion of Eq. (42) is

$$\log \langle e^{\beta F} \rangle = \sum_{n=1}^{\infty} M_n \beta^n / n! \tag{49}$$

For simplicity we consider first the case where only pair interactions contribute to F; the extension to include higher-order interactions will be very simple. In the nth semi-invariant occurs

$$\langle F^n \rangle = (\sum_{\{\mathbf{N}_2\}} [F^n \prod_{r=1}^{\phi} \prod_{i,j,\subset N_2^r} (1 + h_{ij})]) / (\mathbf{B}^{\mathbf{N}_2})^* \tag{50}$$

Every term in the expansion of the right-hand side of Eq. (50) can be represented by a diagram in which each defect whose coordinates appear in the term is represented by a circle (*node*), and in which each $F^{(2)}$ function containing the coordinates of a given pair of defects is represented by a full line joining the corresponding nodes. The pair of defects is then said to be *directly connected* by an $F^{(2)}$-bond. A pair of nodes may be *indirectly connected* through one or more intermediate nodes. In a similar manner we represent each h function in a term by a corresponding dotted line on the diagram. When a node is connected to another node by two, three, or more paths, either directly or through mutually exclusive sets of intermediate nodes, then the pair of nodes is said to be doubly, triply, or in general *multiply connected*.

Consider first the evaluation of terms not involving h functions. The diagrams may be classified according to their topology into

three classes: (a) unlinked diagrams in which each diagram falls into two or more separate parts, the nodes of the separate parts being unlinked by any bonds, (b) linked reducible graphs in which each graph can be separated into two or more parts by cutting at one or more nodes (the points of separation are called *articulation points*[63]), (c) linked irreducible graphs in which every node is multiply connected (the definition is taken to include the graph of a single line between two nodes). Examples of the three types of graph arising in M_3 are shown in Fig. 2. It is readily shown

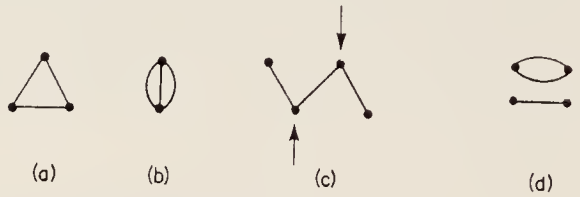

Fig. 2. Some of the diagrams occurring in M_3. Articulation points are indicated by arrows. (a) and (b) are irreducible diagrams; (c) and (d) are linked reducible and unlinked respectively.

that terms corresponding to (a) and (b) can be factored into the product of two or more independent summations. For example, corresponding to the diagrams of Figs. 2c and 2d we have

$$\langle F_{12}F_{23}F_{34}\rangle = \langle F_{12}\rangle\langle F_{23}\rangle\langle F_{34}\rangle \tag{51}$$

$$\langle F_{12}^2F_{34}\rangle = \langle F_{12}^2\rangle\langle F_{34}\rangle \tag{52}$$

The variables that appear in the single parts are therefore statistically independent. By virtue of Eq. (50) it follows that all cross products of linked reducible or unlinked parts must vanish in M_n. In consequence only the irreducible diagrams contribute to M_n. Furthermore, if we consider the contribution of the irreducible diagram in Figs. 2a to M_3 we have the terms

$$\begin{aligned}[\langle F_{12}F_{23}F_{31}\rangle - 3\langle F_{12}F_{23}\rangle\langle F_{31}\rangle \\ + 2\langle F_{12}\rangle\langle F_{23}\rangle\langle F_{31}\rangle] \\ = \langle F_{12}F_{23}F_{31}\rangle + O(1)\end{aligned}$$

The neglected terms are of lower order by a factor of the order of $[(B)^{-1} \times (\text{range of interaction})^3]$. In every M_n only the fully

correlated part contributes.[13] The observations of this paragraph summarize the method of linked clusters.

In the present case in any M_n occur all the irreducibly linked diagrams of n bonds linking k nodes ($2 \leqslant k \leqslant n$). The irreducible diagrams may be classified as either simple irreducible diagrams, in which no two nodes are connected by more than one direct bond, or irreducible diagrams with "melon bonds", in which at least one pair of nodes is connected by two or more direct bonds (see Fig. 2 for examples). Thus, to every simple irreducible diagram there correspond diagrams in higher-order semi-invariants with melon bonds formed by adding more bonds in parallel to existing direct bonds in the simple diagram. The virial expansion is obtained by summing the contributions of all diagrams derived from a particular simple irreducible diagram, and carrying out this process for every simple diagram.

Consider then an irreducible diagram with melon bonds in the nth semi-invariant, consisting of n lines and k nodes whose composition is $\mathbf{k}$. The k nodes can be selected from the $\mathbf{N}_2$ defects in $\binom{\mathbf{N}_2}{\mathbf{k}}$ ways. Let m_{ij} be the number of direct $F^{(2)}$-bonds between nodes i and j. (The labels on the nodes 1, 2, . . . i, j . . . distinguish the nodes from each other and also label the type of defect.) There are $n!/\prod_p m_{ij}!$ ways of dividing n lines among the nodes so that there are specified numbers of direct bonds between pairs of nodes, typically m_{ij} bonds between nodes i and j. $\prod_p$ denotes the product over all pairs of directly connected nodes, and similarly the symbol $\sum_p$ will denote a sum over all such pairs. The total contribution to Eq. (49) from all semi-invariants of all diagrams built from the same simple irreducible diagram as the one considered is therefore

$$\binom{\mathbf{N}_2}{\mathbf{k}} \sum_{n=a}^{\infty} \sum_{\substack{m_{12},m_{23},\ldots=1 \\ (\sum_p m_{ij}=n)}}^{\infty} \frac{\beta^n}{n!} \left(\frac{n!}{\prod_p m_{ij}!} \right) \langle \prod_p (F_{ij}^{(2)})^{m_{ij}} \rangle \qquad (53)$$

where a is the number of bonds in the simple irreducible graph. A similar expression can be written for the contribution of every other simple irreducible graph and its derivative graphs in higher-order semi-invariants. After carrying out the summations in Eq. (53), adding together the contributions from all graphs derived

from simple graphs with k distinguishable nodes of composition $\mathbf{k}$, and summing the resultant expression over all possible compositions of the nodes, the total contribution of all full-line graphs to Eq. (49) is found to be

$$B \sum_{\mathbf{k} \geqslant \mathbf{2}} \mathbf{c}_2^{\mathbf{k}} B_{\mathbf{k}}^* \tag{54}$$

where

$$B_{\mathbf{k}}^* = (B\mathbf{k}!)^{-1} \sum_{\{\mathbf{k}\}} (\sum \prod f_{ij}^{(2)}) \tag{55}$$

$$f_{ij}^{(2)} = \exp(\beta F_{ij}^{(2)}) - 1 \tag{56}$$

$$c_{2s}^r = N_{2s}^r / B^r; \quad \mathbf{c}_2 = \prod_{s=1}^{\omega} c_{2s}^r \tag{57}$$

We have used the fact that

$$\binom{\mathbf{N}_2}{\mathbf{k}} \to \mathbf{N}_2^{\mathbf{k}} / \mathbf{k}!$$

for fixed $\mathbf{k}$ in the limit as $\mathbf{N}_2 \to \infty$ with $\mathbf{c}_2$ fixed. The summand in Eq. (55) is the sum of all simple irreducible diagrams that can be formed among the $\mathbf{k}$ nodes, every bond representing an f_{ij}^2 function. (Thus every node is multiply connected. If $k = 2$ then $B_{\mathbf{k}}^*$ is exceptional and corresponds to the graph of two nodes and an $f^{(2)}$ bond.) It should be noted that $f_{ij}^{(2)}$ is zero when i and j coincide (cf. Eq. (44)).

We now consider the contribution of all diagrams involving h-bonds to Eq. (49). From Eq. (50) it is seen that corresponding to every diagram consisting of n $F^{(2)}$-bonds distributed among $\mathbf{k}$ nodes and occurring in the nth semi-invariant, whether the diagram is unlinked, linked reducible, or irreducible, there is additionally in the same semi-invariant the set of all possible diagrams which can be formed from it by adding h-bonds among the nodes present, with the provisos that only one h-bond can directly link any pair of nodes already directly linked by one or more $F^{(2)}$-bonds and that the h-bonds are only between defects on the same sublattice. In addition we have all the diagrams which can be formed from each of the diagrams of this new set, plus the original diagram containing only $F^{(2)}$-bonds, by first adding in any number of new nodes corresponding to the $(\mathbf{N}_2 - \mathbf{k})$ defects not represented in the original diagram and then adding h-bonds so that

every node is directly connected to at least one other node, with the conditions that no two h-bonds connect the same pair of nodes and that the h-bonds join defects on the same sublattice. All the new diagrams so formed will vanish except those which are irreducibly linked because of the factorization property of the summations involved just as before. However, all such graphs in which an h-bond and one or more $F^{(2)}$-bonds join the same pair of nodes, e.g. Fig. 3a, will give zero contribution by virtue of Eqs.

Fig. 3. Examples of irreducible diagrams making zero contribution.

(43) and (44). Similarly, all diagrams in which two nodes are connected by a single $F^{(2)}$-bond and an h-bond chain will make zero contribution, e.g. Figs. 3b and 3c. The contributions of the non-vanishing irreducible diagrams may be summed by exactly the same procedure as that for diagrams involving only $F^{(2)}$-bonds.

Before quoting the final result it is convenient to transform Eq. (40) to a more convenient form by taking logarithms and applying Stirling's theorem, giving the equation

$$\log Q_0^c = -\log (\mathbf{c}_2^{\mathbf{N}_2}) + \sum_{r=1}^{\phi} \log (1 - c_2^r)^{N_2^r - B^r} \tag{58}$$

where

$$c_2^r = \sum_{s=1}^{\gamma(r)} c_{2s}^r \tag{59}$$

Adding N_2 to the first term and subtracting N_2 from the second term on the right-hand side it is found that

$$\log Q_c^0 = \Big(\sum_{r=1}^{\phi} \{\log (1 - c_2^r)^{N_2^r - B^r} - N_2^r\} \Big) - \log \Big(\prod_{s=1}^{\omega} (c_{2s}^r/e)^{N_{2s}^r} \tag{60}$$

$$= B \sum_{\mathbf{k} \geqslant \mathbf{2}} \mathbf{c}_2^{\mathbf{k}} B_{\mathbf{k}}^h - \log \Big(\prod_{s=1}^{\omega} (c_{2s}^r/e)^{N_{2s}^r} \Big) \tag{61}$$

where $B_{\mathbf{k}}^h$ is defined exactly as for $B_{\mathbf{k}}^*$ but with h_{ij} replacing $f_{ij}^{(2)}$ in the definition. It follows from this definition that $B_{\mathbf{k}}^h$ is zero

unless all of the set $\mathbf{k}$ are on the same sublattice, and that in the latter case the value of $B_{\mathbf{k}}^{h}\mathbf{k}!$ is independent of the composition of the set $\mathbf{k}$. By employing these facts in the first term of the right-hand side of Eq. (61) using the multinomial theorem in the form

$$k! \sum_{\mathbf{k}} \mathbf{c}_2^{\mathbf{k}}/\mathbf{k}! = (c_2^r)^k \quad (k = \text{constant}) \tag{62}$$

for the case where all the defects appearing in $\mathbf{k}$ belong to the same sublattice r, together with a theorem due to Neville[18] which states that

$$\sum_{\{\mathbf{k}\}} (\sum\prod h_{ij})/B^r\mathbf{k}! = -1/k(k-1) \tag{63}$$

when all the defects in $\mathbf{k}$ are on sublattice r, it is straightforward to establish the identity of Eqs. (60) and (61). The second term in Eq. (61) gives minus the Helmholtz free energy divided by kT of a gas of non-interacting particles in which every particle is permitted to occupy any site on its sublattice with equal probability. The first term is a correction to the second arising from the excluded site property.

The first term is conveniently added to the terms in the expansion of $\log Q_c^1$. From Eqs. (39), (54), and (61) together with the analysis following Eq. (57) it is found that

$$\log Q_c = B \sum_{\mathbf{k}\geqslant 2} \mathbf{c}_2^{\mathbf{k}} B_{\mathbf{k}} - \log \left(\prod_{s=1}^{\omega} (c_{2s}^r/e)^{N_{2s}^r}\right) \tag{64}$$

where $B_{\mathbf{k}}$ is defined by

$$B_{\mathbf{k}} = \sum_{\{\mathbf{k}\}} (\sum\prod f_{ij})/B\mathbf{k}! \tag{65}$$

$$f_{ij} = f_{ij}^{(2)} + h_{ij} \tag{66}$$

The summand of Eq. (65) is of all multiply connected diagrams of f-functions on the vertices of the set $\mathbf{k}$. Using the definitions of Eqs. (65)–(66) we have the set of all multiply connected diagrams among $\mathbf{k}$ nodes made up of $f^{(2)}$-bonds and h-bonds, the latter connecting only defects on the same sublattice. In using this compact notation, it must be remembered that all diagrams in which two vertices are directly linked by an $f^{(2)}$-bond and also either a single h-bond or an h-bond chain always give zero contribution.

It remains to extend the result to the case of higher-order interactions between the defects. The calculation may be repeated retaining all the terms in the expansion (33). The diagram representation can conveniently be extended by representing each interaction $[F^{(n)}(\{\mathbf{n}\})]^m$ involving n defects as a shaded area on the diagram with vertices coinciding with the set of $\mathbf{n}$ nodes and the power of the interaction m written inside the area with a circle around it. Examples are shown in Fig. 4. In the semi-

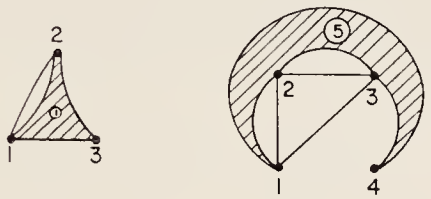

Fig. 4. Examples of diagrams involving higher-order interactions: (a) $F^{(3)}(\{1, 2, 3\})$ $F^{(2)}(\{1, 2\})$, (b) $F^{(2)}(\{1, 2\})$ $F^{(2)}(\{2, 3\})$ $F^{(2)}(\{3, 1\})$ $F^{(4)}(\{1, 2, 3, 4\})^5$.

invariant expansion we now have additional diagrams involving the higher-order interactions. The previous classification of diagrams can be used. Once more only multiply connected diagrams contribute and the summations can be carried out. Cluster functions are defined by the equation

$$f_{\mathbf{n}}^{(n)} = \exp(\beta F^{(n)}(\{\mathbf{n}\})) - 1 \tag{67}$$

Then the previous result (Eqs. (64)–(65)) is unchanged except that the summand in B_k is now the sum of all multiply connected diagrams on $\mathbf{k}$ nodes formed from the cluster functions $f^{(2)}$, $f^{(3)}$, ..., $f^{(k)}$ plus the h functions such that no two $f^{(n)}$-bonds join exactly the same n nodes in any diagram. (The $\mathbf{k}$ nodes are distinguishable, and if all the defects of $\mathbf{k}$ are of different species every diagram makes a different contribution to $B_{\mathbf{k}}$. If some or all of the defects are of the same species then some of the diagrams become degenerate, but all the degenerate diagrams contribute to $B_{\mathbf{k}}$.) The interaction energies $F^{(n)}$ appearing in Eq. (67) are all zero when two of the defects of $\mathbf{n}$ are on the same site.

B. Other Thermodynamic Functions

Once the cluster expansion of the partition function has been made the remaining thermodynamic functions can be obtained as cluster expansions by taking suitable derivatives. Of particular interest are the expressions for the equilibrium concentrations of intrinsic point defects for the various types of lattice disorder. Since the partition function is a function of $\mathbf{N}_1$, $\mathbf{N}_2$, V, and T, it is convenient for the derivation of these expressions to introduce defect chemical potentials for each of the species in the set $(\mathbf{N}_1 + \mathbf{N}_2)$ defined, by analogy with ordinary Gibbs chemical potentials (cf. Section I), by the relation

$$\begin{aligned} \bar{\mu}^r_{is} &= \left(\frac{\partial F}{\partial N^r_{is}}\right)_{T,V,N^t_{ju}\neq N^r_{is}} \quad (i = 1, 2) \\ &= \left(\frac{\partial G}{\partial N^r_{is}}\right)_{P,T,N^t_{ju}\neq N^r_{is}} \end{aligned} \tag{68}$$

G is the total Gibbs free energy of the crystal. The condition for equilibrium is that the Gibbs free energy is a minimum,

$$(dG)_{T,P,\mathbf{N}} = \sum_{s=1}^{\delta} \bar{\mu}^r_{1s} dN^r_{1s} + \sum_{t=1}^{\omega} \bar{\mu}^r_{2t} dN^r_{2t} = 0 \tag{69}$$

where δ and ω are the total numbers of species in sets $\mathbf{N}_1$ and $\mathbf{N}_2$ respectively. There are certain restrictions on this condition since all the N's appearing here are not independent. Since the system considered is closed there are restrictions of the form

$$0 = \sum_{s}^{(0u)} dN^r_{1s} + \sum_{t}^{(0u)} dN^r_{2t} \quad (u = 1, 2, \ldots, \sigma) \tag{70}$$

Here the summations are over all species in sets $\mathbf{N}_1$ and $\mathbf{N}_2$ which correspond to the presence of atoms of chemical species u, which is one of the σ species occurring in the perfect crystal (cf. Eq. (5)). Similarly, for the ν kinds of impurity atom we have the relations

$$0 = \sum_{s}^{(au)} dN^r_{2s} \quad (u = 1, 2, \ldots, \nu) \tag{71}$$

Note that vacancies are not involved in any of these equations. Further restrictions arise from specifying the crystal structure.

If M^{qr} is the ratio of the number of sites in sublattice number q to the number of sites in sublattice number r, both lattices being one of the θ sublattices occupied by atoms in a perfect crystal, then for the imperfect crystal we have

$$N_{1t}^{q} + \sum_{s_q=1}^{\gamma(q)} N_{2s}^{q} = M^{qr}(N_{1u}^{r} + \sum_{s_r=1}^{\gamma(r)} N_{2s}^{r}) \tag{72}$$

where N_{1t}^{q} is the number of "right" atoms on sublattice number q (by definition they can be of only one kind) and the notation of Eq. (15) has been used in writing the summations. Differentiation yields a further relation between the dN's. Another restriction arises from the condition of electrical neutrality for the crystal,

$$0 = \sum_{s=1}^{\delta} e_{1s}^{r} dN_{1s}^{r} + \sum_{t=1}^{\omega} e_{2t}^{r} dN_{2t}^{r} \tag{73}$$

e_{is}^{r} is the charge on species is on sublattice number r. (This is a real not an "effective" charge. For example it is $+2e$ for a Cd^{2+} ion in NaCl but zero for a cation vacancy in this, or any other, system.) Finally, there may be further conditions involved in the statement of the type of disorder present and not already implicit in Eqs. (70)–(73) above. For example, for Frenkel disorder in a one-component system of neutral atoms one must specify that the number of interstitials is equal to the number of vacancies. (For Frenkel disorder in an ionic crystal however this yields nothing not already given by Eqs. (70–(73)).

By taking the minimum in Eq. (69) subject to the restrictions specified and using Lagrange undetermined multipliers (see, for example, Ref. 6), one finds a set of relationships satisfied by the defect chemical potentials. The results for the three basic types of intrinsic lattice disorder are as follows:

(a) For vacancy disorder in a pure metal, M, as well as in a dilute alloy

$$\bar{\mu}_{2v} = 0 \tag{74a}$$

(b) For interstitial disorder in a pure metal, M, as well as in a dilute alloy

$$\bar{\mu}_{1\mathrm{M}} = \bar{\mu}_{2i} \tag{74b}$$

The subscripts M and i refer to metal atoms in their normal and in interstitial sites respectively.

(c) For antistructure disorder in a compound AB

$$\bar{\mu}^{\mathrm{B}}_{1\mathrm{B}} + \bar{\mu}^{\mathrm{A}}_{1\mathrm{A}} = \bar{\mu}^{\mathrm{A}}_{2\mathrm{B}} + \bar{\mu}^{\mathrm{B}}_{2\mathrm{A}} \tag{74c}$$

(d) The results for the various hybrid types of disorder follow similarly. Of particular interest is the case of both Schottky and cationic Frenkel disorder occurring in a uni-univalent salt, MX, which may contain a substitutional impurity IX_2. The result is

$$\bar{\mu}_{2+} = -\bar{\mu}_{2-} = \bar{\mu}_{\mathrm{IM}} - \bar{\mu}_{2i} \tag{74d}$$

where the subscripts + and − refer to cation and anion vacancies respectively.

The general expressions for the defect chemical potentials are found from Eqs. (30)–(35) and (64) and the definition (68). For the defect species one finds that

$$\bar{\mu}^r_{2s} = F^r_{2s} + kT \log (c^r_{2s}\gamma^r_{2s}) \tag{75}$$

where the activity coefficient defined here has the expansion*

$$\log \gamma^r_{2s} = -\frac{1}{\alpha^r}\left(\frac{\partial S}{\partial c^r_{2s}}\right)_{\mathbf{B}} + \log c^r_{1t}\gamma^r_{1t} \tag{76}$$

where

$$\alpha^r = B^r/B \tag{77}$$

and the sum S is defined by

$$S = \sum_{\mathbf{n}\geqslant\mathbf{2}} \mathbf{c}_2^{\mathbf{n}} B_{\mathbf{n}} = \sum_{\mathbf{n}\geqslant\mathbf{2}} \frac{\mathbf{c}_2^{\mathbf{n}}}{B\mathbf{n}!} \sum_{\{\mathbf{n}\}} R(\mathbf{n}) \tag{78}$$

$B_{\mathbf{n}}$ is the cluster function defined previously and the last equation defines the cluster sum $R(\mathbf{n})$. For species in the set $\mathbf{N}_1$ it is found that

$$\bar{\mu}^r_{1s} = F^r_{01s} + kT \log (c^r_{1s}\gamma^r_{1s}) \tag{79}$$

* The second term on the right-hand side of Eq. (76) is the logarithm of the activity of the species of atom which would occupy the defect site in the pure crystal. From Eq. (80) we see that this is essentially the partial pressure of the lattice gas of all the defects on the sublattice occupied by the defect, the crystal being treated as incompressible. It is thus similar to the osmotic correction which must be applied to activity coefficients calculated in the McMillan–Mayer solution theory.[58,64] At low concentrations the contribution to $\log\gamma^r_{2s}$ is negligible and it has been systematically neglected throughout the remainder of this paper and in Ref. 4.

where the activity coefficient defined here has the expansion

$$\log \gamma_{1s}^r c_{1s}^r = -B\left(\frac{\partial S}{\partial B^r}\right)_{\mathbf{N}_2} - c_2^r \tag{80}$$

By combining these expressions for defect chemical potentials and coefficients with the relations between the chemical potentials at equilibrium (for example Eqs. (74)) explicit expressions are obtained for the defect concentrations at equilibrium which are quite analogous to the quasi-chemical results (Section IV- A) apart from the presence of the activity coefficients. We consider examples of these equations in later sections.

In considering the equilibrium of the crystal with a second phase the Gibbs chemical potentials are required and we therefore express these in terms of the defect chemical potentials so far discussed. The Gibbs free energy of the system is given by

$$G = \sum_{s=1}^{\delta} \bar{\mu}_{1s}^r N_{1s}^r + \sum_{t=1}^{\omega} \bar{\mu}_{2t}^r N_{2t}^r \tag{81}$$

By using the conditions for thermodynamic equilibrium (e.g. Eqs. (74)) to simplify the equation and by the use of the relations (cf. Eqs. (70) and (71))

$$\begin{aligned} N_{0u} &= \sum_{s}^{(0u)} N_{1s}^r + \sum_{t}^{(0u)} N_{2t}^r \\ N_{au} &= \sum_{s}^{(au)} N_{2s}^r \end{aligned} \tag{82}$$

and the various relationships arising from crystal structure, electrical neutrality, and defect structure noted above, the numbers of sets $\mathbf{N}_1$ and $\mathbf{N}_2$ can be eliminated in favour of the thermodynamic variables of $\mathbf{N}_0$ and $\mathbf{N}_a$ and the resulting equation compared with the equation

$$G = \sum_{s=1}^{\sigma} N_{0s}\mu_{0s} + \sum_{t=1}^{\nu} N_{as}\mu_{as} \tag{83}$$

to obtain the relationship between the Gibbs chemical potentials and the defect chemical potentials. For example, for the systems described by Eqs. (74) it is found that for both (a) and (b)

$$\mu_{0\mathrm{M}} = \bar{\mu}_{1\mathrm{M}} \tag{84}$$

for case (c)

$$\mu_{0A} = \bar{\mu}_{1A}^{A}, \quad \mu_{0B} = \bar{\mu}_{1B}^{B} \tag{85}$$

for case (d)

$$\mu_{0M} = \bar{\mu}_{1M}, \quad \mu_{0X} = \bar{\mu}_{1X}$$

$$\mu_{aI} = \bar{\mu}_{2I} + \bar{\mu}_{2+} \tag{86}$$

The discussion throughout this paper assumes that the system is homogeneous. However, in ionic crystals if the formation energies of the oppositely charged defects are not equal then in the surface layer of the crystal a space-charge layer is formed due to an excess of one sort of defect. The layer is quite analogous to the familiar diffuse layer at aqueous salt–electrode interfaces in electrochemistry. The difference in potential between the bulk and surface layers is of importance if one wishes to equate the chemical potential of an ion in the bulk of the crystal with its chemical potential in a second phase, since one must add to the chemical potential appearing above (e.g. in Eq. (86)) an additional quantity equal to the charge on the ion multiplied by the potential difference. The latter is readily calculated in terms of defect properties[1,6,35] and we shall not discuss this complication any further. The cluster formalism can be extended to the case of such non-uniform systems[1] but we shall not discuss this here.

C. Defect Distribution Functions and Potentials of Average Force

The distribution function for the probability that if we examine a system of our ensemble, we shall find any n_{21}^{r} defects of species one (out of N_{21}^{r}), . . ., any n_{2s}^{r} defects of species s (out of N_{2s}^{r}) in the configuration $\{\mathbf{n}_2\}$ is

$$\rho^{(\mathbf{n}_2)}(\{\mathbf{n}_2\}) = \frac{\mathbf{N}_2!}{(\mathbf{N}_2 - \mathbf{n}_2)!} \times \frac{\sum'_{\{\mathbf{N}_2 - \mathbf{n}_2\}} \exp(\beta F(\{\mathbf{N}_2\}))}{\sum'_{\{\mathbf{N}_2\}} \exp(\beta F(\{\mathbf{N}_2\}))} \tag{87}$$

Just as in the solution theory, it is convenient to define correlation functions by the equation

$$\rho^{(\mathbf{n}_2)}(\{\mathbf{n}_2\}) = \mathbf{c}_2^{\mathbf{n}_2} g^{(\mathbf{n}_2)}(\{\mathbf{n}_2\}) \tag{88}$$

and a potential of mean force by the relation

$$\log g^{(\mathbf{n}_2)}(\{\mathbf{n}_2\}) = \beta w^{(\mathbf{n}_2)}(\{\mathbf{n}_2\}) \tag{89}$$

The cluster expansions of the correlation functions and potentials of mean force can be found by studying the semi-invariant expansion of $\log g(\{\mathbf{n}\})$ and by the use of the linked cluster theorem. The method is a straightforward extension of those given in the preceding section and dctails can be found in the paper by Allnatt and Cohen.[3] The linked cluster method is simpler and

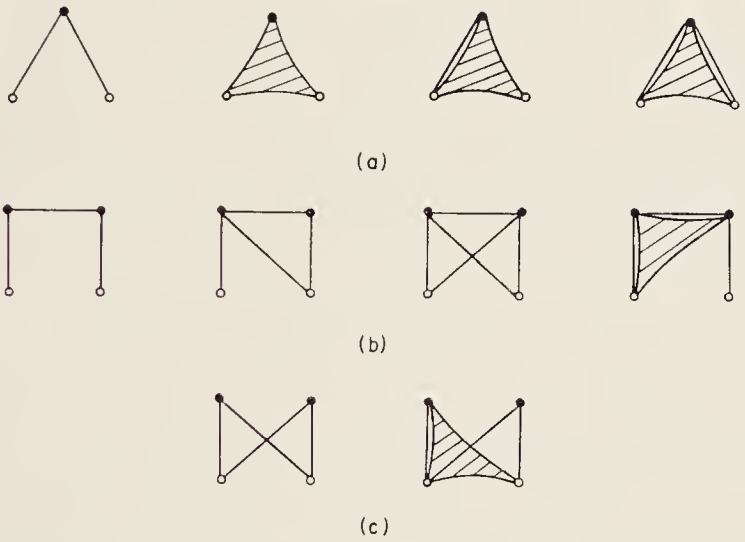

Fig. 5. Examples of products occurring (a) in $P(ij\colon \mathbf{1})$ and $Q(ij\colon \mathbf{1})$, (b) in $P(ij\colon \mathbf{2})$ and $Q(ij\colon \mathbf{2})$, (c) in $P(ij\colon \mathbf{2})$ but *not* $Q(ij\colon \mathbf{2})$.

also more easily generalized to include the non-pairwise interactions than the methods first used to obtain the corresponding imperfect gas expressions. The final result is

$$\begin{aligned}\log g^{(\mathbf{n})}(\{\mathbf{n}\}) &= \beta F(\{\mathbf{n}\}) + \sum_{\mathbf{m}\geqslant \mathbf{1}} \frac{\mathbf{c}^{\mathbf{m}}}{\mathbf{m}!} \sum_{\{\mathbf{m}\}} Q(\mathbf{n}:\mathbf{m}) \\ &= \beta w^{(\mathbf{n})}(\{\mathbf{n}\})\end{aligned} \tag{90}$$

$Q(\mathbf{n}:\mathbf{m})$ is defined as the sum of all products of cluster functions (defined by Eq. (67)) and of all products of cluster functions and h-functions such that:

(a) there are no bonds which connect only nodes of the set $\mathbf{n}$,

(b) all the nodes of the set **m** are connected among themselves independently of the set **n**,

(c) every node of **m** is connected to at least two of the set **n** by independent paths,

(d) the h-bonds connect only nodes of which the corresponding defects lie on the same sublattice (which restriction is included in the definition of h_{ij}).

Note that the definition excludes diagrams composed solely of h-bonds. Also we have

$$g^{(\mathbf{n})}(\{\mathbf{n}\}) = \exp(\beta F(\{\mathbf{n}\}))\left\{1 + \sum_{\mathbf{m}\geqslant \mathbf{1}} \frac{\mathbf{c}^{\mathbf{m}}}{\mathbf{m}!} \sum_{\{\mathbf{m}\}} P(\mathbf{n}:\mathbf{m})\right\} \qquad (91)$$

The definition of $P(\mathbf{n}:\mathbf{m})$ is identical with that of $Q(\mathbf{n}:\mathbf{m})$ except that condition (b) is to be omitted. (In writing these equations, and in many of those that follow, we can omit the subscript 2 since no ambiguity will arise in practice.) Examples of products occurring in $Q(\mathbf{n}:\mathbf{m})$ and $P(\mathbf{n}:\mathbf{m})$ are shown in Fig. 5.

D. Specialized Distribution Functions

In describing the defect distribution it is frequently convenient to use certain special distribution functions which are related to those defined above. For example, in ionic crystals one is frequently interested in the properties of nearest-neighbour complexes of an impurity ion and a cation vacancy (cf. Section IV-A). However, one is generally interested not in the simple probability of finding such a nearest-neighbour pair, which is given by $\rho^{(2)}$, but in the probability of finding such a pair with the condition that there is no other defect which is a nearest neighbour to either member of the pair. This probability must clearly involve higher distribution functions as well as $\rho^{(2)}$.

The required specialized distribution functions are quite analogous to those which are currently of interest in the theory of fluids with short-range intermolecular forces (see Squire and Salsburg[81] and references therein). We require the probability that a set **n** of defects shall be in a configuration $\{\mathbf{n}\}$ with the restriction that none of the remaining $(\mathbf{N} - \mathbf{n})$ defects are on a particular set of sites **b** out of the total **B** sites of the crystal. This probability may be written as

$$\rho^{(\mathbf{n})}(\{\mathbf{n}\};\ \mathbf{B}-\mathbf{b}) = \frac{\mathbf{N}!}{(\mathbf{N}-\mathbf{n})!}\sum_{\{\mathbf{N}-\mathbf{n}\}}^{(\mathbf{B}-\mathbf{b})}\rho^{(\mathbf{N})}(\{\mathbf{N}\}) \tag{92}$$

The summation is over all configurations of the $(\mathbf{N}-\mathbf{n})$ defects on the $(\mathbf{B}-\mathbf{b})$ sites, the remaining $\mathbf{n}$ defects being fixed in the configuration $\{\mathbf{n}\}$. The summation may be written as

$$\sum_{\{\mathbf{N}-\mathbf{n}\}}^{(\mathbf{B}-\mathbf{b})} = \sum_{\mathbf{k}=\mathbf{0}}^{\mathbf{N}-\mathbf{n}}\binom{\mathbf{N}-\mathbf{n}}{\mathbf{k}}(-)^{k}\sum_{\{\mathbf{k}\}}^{(\mathbf{b})}\sum_{\{\mathbf{N}-\mathbf{n}-\mathbf{k}\}}^{(\mathbf{B})} \tag{93}$$

from which we find that

$$\rho^{(\mathbf{n})}(\{\mathbf{n}\};\ \mathbf{B}-\mathbf{b}) = \sum_{\mathbf{k}=\mathbf{0}}\frac{(-)^{k}}{\mathbf{k}!}\sum_{\{\mathbf{k}\}}^{(\mathbf{b})}\rho^{(\mathbf{n}+\mathbf{k})}(\{\mathbf{n}+\mathbf{k}\};\ \mathbf{B}) \tag{94}$$

In solution theory the specialized distribution functions of this kind should appear in the theory of ion pairs in ionic solutions, and a form of the Bjerrum–Fuoss ionic association theory adapted to a discrete lattice is generally used for the treatment of the complexes in ionic crystals mentioned above. In fact, the above equation is not used in this treatment. Comparison of the two procedures is made in Section VI-D.

V. SHORT-RANGE INTERACTIONS

In the remaining sections we review some of the equations of practical importance which can be obtained from the formal cluster expansions. It is convenient to distintuish between systems with short-range interactions involving only nearest- and next-nearest-neighbour interactions and systems involving Coulombic interactions between defects. Many of the results for short-range interactions will already be familiar as they are slightly more precise statements of equations generally obtained using the law of mass action (see, for example, Ref. 37). However, derivation from the cluster expansions has the advantage that the approximations made can be more precisely stated. The equations for many-defect systems and the inclusion of second- as well as first-neighbour interactions are at once apparent in this scheme but tedious to derive otherwise.

In writing explicit results an extension of the notation is useful. $f_{ij}^{(2)}(\{i_s j_r\}_n)$ is the $f^{(2)}$ cluster function for defects number i and j

which are of kinds s and r respectively. The subscript n denotes that in the particular configuration they are n-th nearest neighbours. $\phi_n(sr)$ is the number of lattice sites of the kind occupied by a defect of type r which are n-th nearest neighbours to a site of the kind occupied by defects of type s. The subscripts v and i denote vacancies and interstitials respectively. Only nearest-neighbour interactions will be retained unless otherwise stated.

A. Dilute Single-Defect Systems

The systems we have in mind here are pure monatomic solids such as metals and inert gas solids which contain only one kind of defect in a single electronic state. We consider only vacancies explicitly, but rather similar expressions hold for systems containing only interstitials. From Eqs. (74a) and (75) we find that at equilibrium

$$\begin{aligned} c_v &= (\gamma_v)^{-1} \exp(\beta F_v) \\ &= \exp(\beta F_v)\,[1 + 2B_2 c_v + (3B_3 + 2B_2^2)\, c_v^2 + \ldots] \end{aligned} \tag{95}$$

where the exponential in the expression for the activity coefficient has been expanded and only terms up to the order of c_v^2 retained. For nearest-neighbour interactions only we have

$$B_2 = \tfrac{1}{2}\{\phi_1(\exp[\beta F^{(2)}(\{1_v 2_v\}_1)] - 1) - 1\} \tag{96}$$

and the definition of B_3 is

$$B_3 = \sum_{\{1,2,3\}} (f_{123}^{(2)}[1 + f_{12}]\,[1 + f_{13}]\,[1 + f_{23}] + f_{12}f_{23}f_{31})/6B \tag{97}$$

The quantity c_v is, of course, the *total* concentration of vacancies including those involved in nearest-neighbour vacancy pairs or in higher aggregates.

In pure metals the properties of intrinsic vacancies have been studied recently both by equilibrium measurements and by a variety of experiments in which the defects are quenched in the metal and studied at lower temperatures. The mass action formalism has been used to describe the results in terms of free vacancies, vacancy pairs, and trivacancies. For noble metals at equilibrium higher aggregates appear to be unimportant. The mass action equations may be compared with the one above.

For example, the equilibrium measurements of linear thermal expansion and X-ray lattice expansion of Simmons and Baluffi[80] yield directly the total concentration of vacancies, and this is written as

$$c_v = c_v^0 + 2c_p + 3c_t + \ldots \tag{98}$$

where c_p and c_t are the concentrations of di- and trivacancies respectively and c_v^0 the concentration of free vacancies. Using the law of mass action we have

$$c_v^0 = \exp(\beta F_v) \tag{99}$$

$$c_p = \tfrac{1}{2}(c_v^0)^2 \phi_1 \exp(\beta F^{(2)}(\{1_v 2_v\}_1)) \tag{100}$$

$$c_t = (c_v^0)^3 \sum_i y_i \exp(\beta F(\{123\}^i)) \tag{101}$$

The summation in the last expression is over all different configurations, $\{123\}^i$, of three defects, each one being within nearest-neighbour distance of at least one other, and y_i is a geometric factor. (For example, four configurations of a trivacancy can be drawn for a face-centred cubic lattice. In only one of these

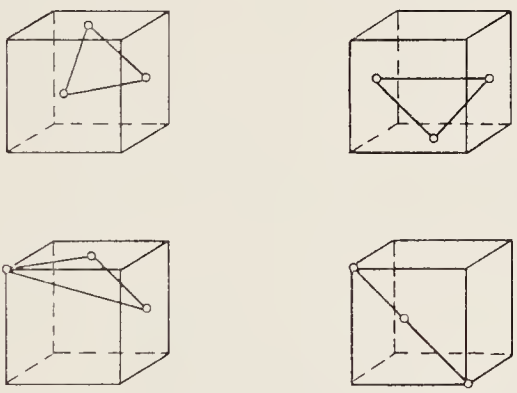

Fig. 6. Configurations of a trivacancy in an f.c.c. lattice.

configurations are all three vacancies nearest neighbours. However, calculations by Dienes and Damask[19] and by Vineyard[84] suggest that in the lowest energy form this configuration distorts to a tetragonal form in which the atom equidistant from all three vacancies is displaced towards them so that there is a tetrahedron of four vacancies with an atom at the centre.) Comparison of Eqs.

(98) and (95) shows that the terms of order $(c_v^0)^2$ are the same provided that

$$\exp(\beta F^{(2)}) \gg 1$$

For example, at 1200°K $-F^{(2)}$ must be greater than 0.24 eV in order that the two correction terms differ by less than 10%. However, for the small defect concentrations of interest here (e.g. $c_v \approx 6 \times 10^{-5}$ for $F_v = 1.0$ eV in copper) the correction due to the vacancy-pair term is unimportant for much smaller values of $-F^{(2)}$ so that differences are not practically very important. The terms of order $(c_v^0)^3$ are more difficult to compare and the numerical values depend on the relative magnitudes of $F^{(2)}$ and $F(\{123\})$, as can be seen by noting that the sum of products of f-functions in B_3 is equivalent to

$$\exp(\beta F(\{123\})) - [f_{12}f_{13} + f_{12}f_{23} + f_{23}f_{31} + f_{12} + f_{23} + f_{31} + 1]$$

whereas the mass action expression (Eq. (102)) does not involve the term in square brackets or excluded volume contributions like those in which two defects are assigned to the same site in evaluating the cluster functions. However, the trivacancy term makes only a very small contribution to the measured quantity in the equilibrium experiments. It is worth noting that non-pairwise interactions appear to be important. For example, according to calculations by Vineyard $-F(\{123\})$ is 0.46 eV for the tetragonal form of trivacancy whereas $-F^{(2)}$ is 0.06 eV, so that $F^{(3)}(\{123\})$ is 0.28 eV in this case. The many experimental and theoretical estimates of divacancy and trivacancy binding energies in copper and other metals are, however, in quite poor agreement at present (see e.g. Simmons and Baluffi[80]) and we shall not consider these systems further. When accurate values are available it may be necessary to proceed in a consistent manner by using the cluster expansion expressions for defect concentrations and distribution functions.

The concentrations of the various aggregates, divacancies, trivacancies, etc. can of course be written down, although these do not appear in our expression for c_v. For example, if a divacancy is defined as a nearest-neighbour pair of vacancies neither of which has a second vacancy as nearest neighbour to it, then the concentration of such divacancies is $\phi_1/2$ multiplied by $\rho^{(2)}(\{1_v 2_v\}_1;$

B — b). The distribution function is defined in Section IV-4 and **b** now denotes the sites which are nearest neighbours to the two vacancies. From Eq. (94) it is seen that

$$c_p = \tfrac{1}{2}\phi_1[(c_v)^2 g^{(2)}(\{1_v 2_v\}_1) - (c_v)^3 \sum_{\{3_v\}}^{(\mathbf{b})} g^{(3)}(\{1_v 2_v\}_1\{3_v\}) + O(c_v^4) \ldots] \quad (102)$$

and by using the cluster expansions for the correlation functions of Eq. (91) it is found that to terms of order $(c_v)^3$

$$c_p = \tfrac{1}{2}\phi_1(c_v)^2 \exp(\beta F^{(2)}(\{1_v 2_v\}))\,[1 - c_v \sum_{\{3\}}^{(\mathbf{b})} (1 + f_{13} + f_{23})] \quad (103)$$

The term in square brackets provides a correction to the mass action expression which is clearly negligible in most circumstances.

B. Dilute Many-Defect Systems

The most important application to be considered under this heading is the calculation of intrinsic defect concentrations in dilute solid solutions. If the solution is so dilute that only the leading terms in the various cluster expansions need be retained then the results required are slight generalizations of those above and follow at once from the notation for the general results. For example, the equilibrium concentration of vacancies in a dilute solution of a single solute, s, is found from Eqs. (74a) and (75) to be

$$c_v = \exp(\beta F_v)\,[1 + c_v\phi_1(\exp[\beta F^{(2)}(\{1_v 2_v\}_1)] - 1) - c_v + c_s\phi_1(\exp[\beta F^{(2)}(\{1_v 3_s\}_1)] - 1) - c_s] \quad (104)$$

neglecting all but nearest-neighbour terms and terms of order c^2. A situation of frequent interest is when vacancy–vacancy and solute–solute interactions are small but there is a large solute–vacancy binding energy. If we assume also that $c_s \gg c_v$ (but not so large that higher virial coefficients have to be considered) then

$$c_v = \exp(\beta F_v)\,[1 + c_s\phi_1 \exp(\beta F^{(2)}(\{1_v 3_s\}_1)) - c_s(\phi_1 + 1)] \quad (105)$$

which is the same as the expression given by Lomer[55] (apart from the presence of $(\phi_1 + 1)$ instead of ϕ_1 in the last term) and generally derived by the law of mass action. The expression has been used in the discussion of solute diffusion and of measurements of vacancy concentrations in dilute aluminium–silver alloys by the linear thermal expansion–X-ray expansion method.[8] The concentration of nearest-neighbour solute–vacancy complexes found from the distribution functions just as for the divacancy again agrees with that found by the law of mass action (cf. Howard and Lidiard,[37] Eq. (III. 3.16)) if only the terms of lowest order in c_v and c_s are retained.

C. Further Remarks

The rather brief examples above should suffice to illustrate that for dilute systems with short-range interactions expressions for concentrations of point defects or defect aggregates are readily obtained by retaining the first two or three virial coefficients in the relevant expansions. Compared with the quasi-chemical (mass action) formalism traditionally employed the method has the advantages of precision and compactness of statement and the relative ease with which many-defect systems and more distant interactions can be dealt with. More complex kinds of disorder than those discussed above, such as Schottky–antistructure disorder (cf. Section I), introduce no new features. A more important case is that of the antistructure disorder which is possible if the sizes and electronegativities of the atoms in a compound are not very dissimilar (e.g. Bi_2Te, Mg_2Sn). The equilibrium condition has already been given (Eq. (74c)). A limiting case of antistructure disorder is provided by the order–disorder alloys, where the degree of disorder increases rapidly as the temperature is raised to a critical temperature T_c. Above T_c the separate sublattices are no longer distinguishable. Special methods are available for this famous statistical problem;[20,30,67] the formalism so far discussed is not meant for such crystals. Similarly, large departures from stoichiometry (see Section I), which are often dealt with by the order–disorder techniques,[7,71] do not lie within its scope. There are at least two essential features absent in the application of the simplest order–disorder

theories to crystals with relatively large deviations from stoichiometry. The first is the absence of non-pairwise interactions (see Eq. (33)), which must be relatively important at high defect concentrations. The second is the absence of an adequate treatment of the dependence of the lattice vibrations on the stoichiometry. The latter is of course well known to be important in the classical application of order–disorder theories to alloys though the progress made is not very great. In Section VII we call attention to the framework proposed by Mayer for the discussion of such systems. However, the computations required in this scheme are heavy and it remains to be seen just how complicated a defect system it will prove possible to treat.

Having familiarized ourselves slightly with the cluster expansions let us now look in detail at a more difficult example involving long-range interactions where the quasi-chemical formalism appears less satisfactory.

VI. COULOMB INTERACTIONS

A. Introduction

In this section we are concerned with the properties of intrinsic Schottky and Frenkel disorder in pure ionic conducting crystals and with the same systems doped with aliovalent cations. As already remarked in Section I, the properties of uni-univalent crystals, e.g. sodium choride and silver bromide which contain Schottky and cationic Frenkel disorder respectively, doped with divalent cation impurities are of particular interest. At low concentrations the impurity is incorporated substitutionally together with an additional cation vacancy to preserve electrical neutrality. At sufficiently low temperatures the concentration of intrinsic defects in a doped crystal is negligible compared with the concentration of added defects. We shall first mention briefly the theoretical methods used for such systems and then review the use of the cluster formalism.

The statistical mechanics of such impurity systems has been treated by Lidiard[51,53] and his method has been widely employed in the interpretation of experimental data, e.g. ionic conductivity,[5,51] dielectric loss,[8] thermoelectric power,[16,35] diffusion,[31]

and paramagnetic resonance of impurity ions.[86] The problem of interactions of defects in an ionic crystal is clearly similar to that of ions in a solution in that the interactions at more than a few ionic diameters may be adequately described by a Coulombic interaction reduced by the macroscopic dielectric constant, D. However, the dielectric constants of ionic solids are quite small compared with many of the solutions studied in electrochemistry. The experimental studies and theoretical calculations[44,83] suggest that at nearest- and next-nearest-neighbour positions, oppositely charged defect pairs, such as a divalent cation and a cation vacancy, have a binding energy (relative to the infinitely separated defects) which is greater than kT and substantially different from that anticipated for a purely Coulombic attraction. In the treatment of the equilibrium properties of such a system, Lidiard therefore distinguished between an impurity cation and a cation vacancy pair on adjacent lattice sites, called a complex, and the same defects at greater separations. The law of mass action was applied to the equilibrium between "free" defects, whose activity coefficients were taken as equal to the Debye–Hückel values, γ_D, and the neutral complexes, whose activity coefficients were taken as unity. If pairs at greater than nearest-neighbour separation have binding energies appreciably greater than kT, then these are included in the definition of a complex. They are referred to as "excited states" of the complex. The equilibrium constant for the association reaction was taken to be

$$\begin{aligned} K_2 &= \sum_i \phi_i \exp(\zeta_i/kT) \\ &= c_k/c_{+f}c_j\gamma_D^2 \end{aligned} \tag{106}$$

c_k, c_{+f}, c_j are the site fractions (on the cation sublattice) of complexes, "free" vacancies, and "free" impurities. ζ_i is the binding energy of a complex when the components are i-th nearest neighbours, and ϕ_i is the number of such neighbours that a given cation site has. γ_D is the Debye–Hückel activity coefficient

$$\log \gamma_D = -e^2\kappa/2DkT(1 + \kappa R_q) \tag{107}$$

where

$$\kappa^2 = 4\pi e^2(c_{+f}z_+^2 + c_j z_j^2)/DkT\Delta \tag{108}$$

z is the algebraic charge on a defect, Δ the volume of a unit cell of the lattice, and R_q the closest distance to which two oppositely charged defects may approach while still being counted as "free". The procedure is of course analogous to the Bjerrum theory of ion association in electrolyte solutions,[11,18,75] where it has been of great value in the study of solutions of polyvalent electrolytes. (The greater charges on the ions offset the higher dielectric constants of most solutions studied as compared with ionic crystals, so that at small separations the energy of interaction is again appreciably greater than kT.) It is well known that there is a degree of arbitrariness in the definition of an ion pair in the solution theory or of a complex in the defect theory. Bjerrum[11] proposed that any pair of oppositely charged ions at a distance apart less than or equal to $R_q = e^2/2DkT$ should be defined as an ion pair and that ions at a greater separation should be treated as free. This arbitrary definition of R_q, which was dictated largely by mathematical convenience,[12] leads to mathematical and physical difficulties in the theory.[27] Fuoss therefore proposed the alternative definition[27] that if an anion lies in dR at a distance R from a particular cation, then the two shall be called an ion pair provided that no other unpaired anion lies within the sphere of radius R centred on the cation. The ion-pair distribution function $G(R)$, which is defined so that the probability of such an ion pair is $G(R)\,dR$, can be related to the anion–cation radial distribution function and from it can be found the fraction of ion pairs whose members are a distance apart less than or equal to some selected distance. The law of mass action is not used. However, the degree of association calculated in this manner at very high dilution is the same as that calculated from the law of mass action using the equilibrium constant K_2 proposed by Bjerrum. The procedure generally adopted has been to use the mass action formalism with the Bjerrum equilibrium constant at higher concentrations, although this is not consistent with the details of the Fuoss formulation.[73] Poirier and DeLap[70] have recently generalized the Fuoss treatment and corrected an error in the mathematical formulation. However, in the solution theory, vigorous debate still continues as to the merits of various definitions of ion pairs which have been proposed.[29,70] We may note that two distinct starting points are possible: either one studies the theory of

activity coefficients and expects to be able to ascribe a substantial portion of the answer to oppositely charged ions at small distances apart,[28] or one frames the question initially in terms of the study of the radial distribution functions and afterwards proceeds to the study of thermodynamic properties.[29] Both retain arbitrary elements.

Another defect problem to which the ion-pair theory of electrolyte solutions has been applied is that of interactions to acceptor and donor impurities in solid solution in germanium and silicon. Reiss[73,74] pointed out certain difficulties in the Fuoss formulation. His kinetic approach to the problem gave results numerically very similar to that of the Fuoss theory. A novel aspect of this method was that the negative ions were treated as randomly distributed but immobile while the positive ions could move freely.

Among other applications of electrolyte solution theory to defect problems should be mentioned the application of the Debye–Hückel activity coefficients by Harvey[32] to impurity ionization problems in elemental semiconductors. Recent reviews by Anderson[7] and by Lawson[45] emphasizing the importance of Debye–Hückel effects in oxide semiconductors and in doped silver halides, respectively, and the book by Kröger[41] contain accounts of other applications to defect problems. However, additional quantum-mechanical problems arise in the treatment of semiconductor systems and we shall not mention them further, although the studies described below are relevant to them in certain aspects.

Although the theory of solutions has been widely used in formulating problems of defects in solids the problems encountered differ in certain respects. The most obvious point is that defects are restricted to discrete lattice sites, whereas the ions in a solution can occupy any position in the fluid. Sometimes no allowance is made for this fact. For example, it has not been demonstrated that at very low concentrations, in the absence of ion-pair effects, the activity coefficients are identical with those of the Debye–Hückel theory. It can be plausibly argued[51] that at sufficiently low concentrations the effect of discreteness is likely to be negligible, but clearly in developing a theory for any but the lowest concentrations the effect should be investigated. A second point

of difference between the problems in solutions and in solids is that in the case of ionic solutions it is feasible to test the predictions of the theory by measurements of equilibrium thermodynamic properties, i.e. activity coefficients and osmotic coefficients. This will rarely be possible for defects in a solid because of the lack of suitable reversible electrodes. Interest therefore has centred on the interpretation of non-equilibrium properties. Equation (106) has been used to calculate c_k, generally counting only nearest neighbours as complexes. It is assumed that the complexes may be characterized by a diffusion coefficient but that they undergo no net motion in an electric field provided the mean life-time of a complex is sufficiently long.[52] Perhaps the most detailed application of the theory was made by Lidiard,[51] who analysed the conductivity measurements of Etzel and Maurer for the system ($NaCl + CdCl_2$). The "simple association theory" in which Eq. (106) is used with $\gamma_D = 1$ has been much more extensively used (see Refs. 5 and 53 for further references). In some cases the free energy of association, ζ, calculated from the results appears to vary substantially with temperature.[5] The reasons for this are not clear within the framework of the simple association theory. Moreover, the various non-equilibrium properties should, in a rigorous formulation, be linked with the study of the defect distribution functions rather than building round the ion-pair concept right at the start.

In Section VI-B we review a recent attempt to construct an equilibrium theory for ionic defects analogous to the ionic solution theory of Mayer[25,58] starting from the formal expansions for the partition function and distribution functions. It is found that, where necessary, lattice summations can be employed instead of the spatial integrations of solution theory. The thermodynamic properties, and the deviations from ideality which they exhibit in consequence of the long-range Coulomb forces and the short-range forces, are to be understood from the study of the formal cluster expansions rather than a model employing the more arbitrary methods of ionic association theory. In addition, a picture of the deviations of the defect distribution from randomness is to be obtained by a study of the formal expansions for the defect distribution functions and the specialized distribution functions.

B. Activity Coefficients

(1) *Diagram Classification*

For ionic defects the individual terms in the formal virial expansions diverge just as they do in ionic solution theory. The essence of the Mayer theory is a formal diagram classification followed by summation to yield new expansions in which individual terms are finite. The recent book by Friedman[25] contains excellent discussions of the solution theory. We give here only an outline emphasizing the points at which defect and solution theories diverge. Fuller treatment can be found in Ref. 4.

The problem at hand is the evaluation of the activity coefficient defined in Eq. (76). It will be assumed that only pairwise interactions between the defects need be considered at the low defect concentrations we have in mind. (The theory can be extended to include non-pairwise forces.[23]) Then the cluster function $R(\mathbf{n})$ previously defined in Eq. (78) is the sum of all multiply connected diagrams, in which each bond represents an f-function, which can be drawn among the set of $\mathbf{n}$ vertices, the f-function being defined by Eqs. (66), (56), and (43). The Helmholtz free energy of interaction of two defects appearing in this definition can be written as

$$F_{ij}(\mathbf{R}_{ij}) = \frac{z_i z_j e^2}{D R_{ij}} + F_{ij}^{(s)}(R_{ij}) \tag{109}$$

where z_i and z_j are the algebraic charges on defects of kinds i and j, in units of the electronic charge, e. D is the macroscopic dielectric constant of the crystal and its precise significance is further discussed below. $F_{ij}^{(s)}$ is a short-range term arising from deviations from the Coulomb law with macroscopic dielectric constant, together with additional terms arising from the elastic distortion of the lattice when defects are brought close together. $F_{ij}^{(s)}$ is effectively zero at separations of more than a few lattice spacings; theoretical estimates are available for nearest and next nearest separations in some cases.[83] Note that F_{ij} is, apart from constant terms independent of the relative positions of the defects, the change in Helmholtz free energy on adding defects i and j to the crystal so that they are R_{ij} apart, the other defects being considered fixed during this process. (The potential energy of interaction of i and j when the other defects are allowed to relax is the

potential of average force and can be shown to contain a screened Coulomb interaction. It is defined and further discussed below.) The dielectric constant of the crystal, D, is therefore to be measured at frequencies sufficiently high that the defects do not move. Except at temperatures much below the melting point the correct quantity may not always be available experimentally.

By using Eq. (109) in Eq. (66) and expanding the exponential we find that

$$f_{ij} = (k_{ij} + 1)\left(\sum_{n\geq 1}[-\lambda z_i z_j q_{ij}]^n/n!\right) + k_{ij} \tag{110}$$

where

$$k_{ij} = h_{ij} + k_{ij}^* \tag{111}$$

$$k_{ij}^* = \exp[\beta F_{ij}^{(s)}] - 1 \tag{112}$$

$$\lambda = 4\pi e^2/DkT \tag{113}$$

$$q_{ij} = 1/4\pi R_{ij} \tag{114}$$

The terms formed by substituting the expansion of Eq. (110) into Eq. (78) may be represented by diagrams in the manner of Mayer[58] and Meeron.[62] Each product in the summand $R(\mathbf{n})$ can be represented by a diagram of $\mathbf{n}$ labelled vertices. Every function q_{ij} in the product is represented by a solid line between vertices i and j; such a line is called a q-bond. Every function k_{ij} in the product is represented by a dashed line called a k-bond. It follows from the expansion of Eq. (110) and the definition of $R(\mathbf{n})$ that there can be at most one direct k-bond between any pair of vertices in the diagram. The diagrams may be simply represented by symbols according to the following scheme.[62] ν_{ij}^0 signifies that there are ν^0 direct q-bonds between vertices i and j; k_{ij} signifies that there is a direct k-bond between i and j. One k-bond and ν^0 q-bonds all directly connecting i and j are represented by $k\nu_{ij}^0$. Examples of the notation are given in Fig. 7. For example, $(3_{ij}|k_{jk}|k1_{ki})$ denotes a product of three q-bonds between i and j, one k-bond between j and k, and one k-bond plus one q-bond between k and i.

The set of symbols describing the number and location of the bonds among a set of $\mathbf{n}$ vertices, in a diagram representing a product occurring in $R(\mathbf{n})$, is called a pattern[62] and may be represented by the symbol $\tau(\mathbf{n})$. The sum of products $R(\mathbf{n})$ can be

represented as the sum of $R(\tau(\mathbf{n}))$ over all possible patterns $R(\tau(\mathbf{n}))$ which are multiply connected. The patterns may be divided into two classes, namely those diagrams with q-bond chains and those without. (A q-bond chain is a row of vertices each connected to the preceding one and to the following one by a single direct q-bond and connected to no other vertex. A q-bond chain contains at least one intermediate particle with two adjacent q-bonds.) A pattern of m vertices without q-bond chains is called a prototype pattern $\sigma(\mathbf{m})$, and the set of vertices form a prototype set. Any pattern $\tau(\mathbf{N})$ which is not a prototype can be derived

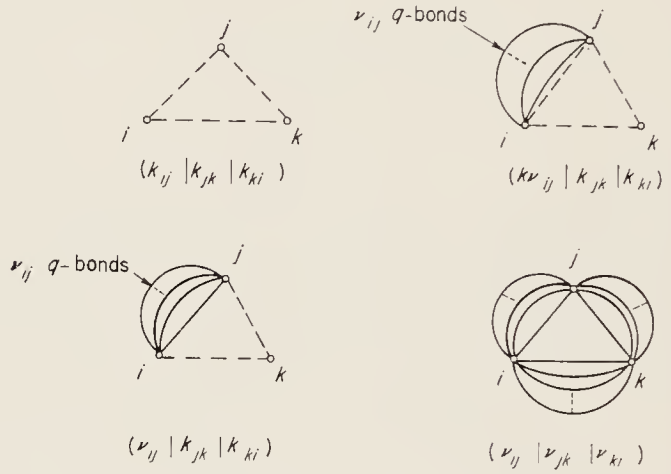

Fig. 7. Diagrammatic representation of some of the products occurring in $R(ijk)$.

from some prototype pattern $\sigma(\mathbf{m})$ ($\mathbf{m} < \mathbf{N}$) by replacing some or all of the q-bonds in the prototype by q-bond chains of suitable lengths. The $\mathbf{N}$–$\mathbf{m}$ vertices in q-bond chains will be designated by $\mathbf{n}$. The ν q-bond chains in a pattern will be designated by the set of numbers 1 to ν. The set $\mathbf{n}$ may be divided into subsets $\mathbf{n} = \mathbf{n}_1 + \ldots + \mathbf{n}_\nu$, where $\mathbf{n}_k$ is the set of vertices in chain number k. In contrast to the solution theory it is convenient to specify the pattern of vertices in each q-bond chain. $\delta(\mathbf{n}_k)$ specifies the order of the $\mathbf{n}_k$ vertices in chain number k. The complete description of a product $R(\tau(\mathbf{n} + \mathbf{m}))$ is given by the symbol $R(\sigma(\mathbf{m}); \delta(\mathbf{n}_1), \ldots, \delta(\mathbf{n}_\nu))$. A special class of patterns is that composed of diagrams which are simple cycles of single

q-bonds. Examples are shown in Fig. 8a. A typical cycle pattern is conveniently designated $R(\delta(\mathbf{n}))$.

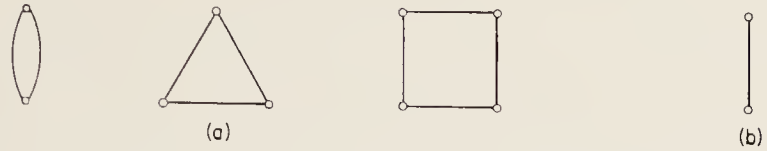

Fig. 8. (a) Diagrams contributing to $S^{(c)}$. (b) Diagram contributing to $S^{(e)}$.

The sum S may be conveniently divided into three contributions

$$S = S^{(c)} + S^{(e)} + S^{(R)} \tag{115}$$

$S^{(c)}$ is the contribution of cycle diagrams (patterns $R(\delta(\mathbf{n}))$; $n \geqslant 2$); $S^{(e)}$ is the contribution of the diagram involving only a single q-bond between two vertices (Fig. 8b); $S^{(R)}$ is the set of remaining diagrams. We consider $S^{(c)}$ in detail to illustrate the method but only outline the derivation of the result for $S^{(R)}$.

(2) *Fourier Transforms and Summations over Cycles*

For $S^{(c)}$ we have

$$S^{(c)} = \sum_{\mathbf{n}\geqslant\mathbf{2}} \frac{\mathbf{c}^{\mathbf{n}}}{B\mathbf{n}!} \sum_{\{\mathbf{n}\}} [\sum \prod (-\lambda q_{ij} z_i z_j)] \tag{116}$$

This infinite sum, each term of which involves a multiple summation, can be converted to an integral over a single variable, and in the continuum limit the value of $S^{(c)}$ obtained yields the Debye–Hückel limiting law activity coefficient. The term appearing in square brackets represents the sum of all multiply connected diagrams, i.e. of all corresponding products of $(-\lambda q_{ij} z_i z_j)$, on a set of $\mathbf{n}$ vertices, the sum being over every distinguishable arrangement of vertices in a cycle, every vertex being labelled and distinguishable. For a given composition, $\mathbf{n}$, vertices occupied by like defects may be interchanged in just $\mathbf{n}!$ ways, so that

$$S^{(c)} = \sum_{\mathbf{n}\geqslant\mathbf{2}} \mathbf{c}^{\mathbf{n}} \sum_{\{\mathbf{n}\}} [\sum'' \prod (-\lambda q_{ij} z_i z_j)]/B \tag{117}$$

The double-primed summation is over all distinguishable arrangements of a set of vertices of fixed composition, **n**, in a cycle, like vertices being treated as indistinguishable.

We now introduce a Fourier transform procedure analogous to that employed in the solution theory.[58,62] For the purposes of the present section a more detailed specification of defect positions than that so far employed must be introduced. Thus, defects i and j are in unit cells l and m respectively, the origins of the unit cells being specified by vectors $\mathbf{R}_l$ and $\mathbf{R}_m$ relative to the origin of the space lattice. The vectors from the origin of the unit cell to the defects i and j, which occupy positions number x and y within the cell, will be denoted $\boldsymbol{\lambda}_i^{(x)}$ and $\boldsymbol{\lambda}_i^{(y)}$; for example, the sodium chloride lattice is built from a unit cell containing one cation site (0, 0, 0) and one anion site ($a/2$, 0, 0), and the translation group is that of the face-centred-cubic lattice. However, if we wish to specify the interstitial sites of the lattice, e.g. for a discussion of Frenkel disorder, then we must add two interstitial sites to the basis at ($a/4$, $a/4$, $a/4$) and ($3a/4$, $a/4$, $a/4$). (Note that there are twice as many interstitial sites as anion–cation pairs but that all interstitial sites have an identical environment.) In our present notation the distance between defects i and j is

$$\begin{aligned}\mathbf{R}_{ij} &= \mathbf{R}_l - \mathbf{R}_m + \boldsymbol{\lambda}_i^{(x)} - \boldsymbol{\lambda}_j^{(y)} \\ &= \mathbf{R}_{lm} - \boldsymbol{\lambda}_{ij}^{(xy)}\end{aligned} \tag{118}$$

The Fourier transform of a function $Y_{ij}(\mathbf{R}_{ij})$, depending on the nature and distance apart of two defects i and j, is defined as

$$\phi_{ij}^{(xy)}(\mathbf{t}) = \sum_m{}' \exp\left[-i\mathbf{t}\cdot(\mathbf{R}_{lm} + \boldsymbol{\lambda}_{ij}^{(xy)})\right] Y_{ij}(\mathbf{R}_{lm} + \boldsymbol{\lambda}_{ij}^{(xy)}) \tag{119}$$

where $\mathbf{t}$ is a vector in the first Brillouin zone of the reciprocal space. The prime on the summation signifies that the summation is over all unit cells m, except that for which $m = l$. The inverse of Eq. (119) is

$$Y_{ij}(\mathbf{R}_{lm} + \boldsymbol{\lambda}_{ij}^{(xy)}) = \left[\frac{\Delta}{(2\pi)^3}\right] \int_{\mathrm{BZ}} d\mathbf{t} \exp\left[i\mathbf{t}\cdot(\mathbf{R}_{lm} + \boldsymbol{\lambda}_{ij}^{(xy)})\right] \phi_{ij}^{(xy)}(\mathbf{t}) \tag{120}$$

Δ is the volume of the unit cell in the direct lattice of the crystal The range of integration is restricted to the first Brillouin zone of the crystal, and the volume of the zone is $(2\pi)^3/\Delta$.

The usefulness of the Fourier transforms lies in the fact that the following convolution theorem can be established.[4] The sum over all configurations of n defects in a chain:

$$S^{(xy)}_{i12\ldots nj}(\mathbf{R}_{ij}) = \sum_{\{\mathbf{n}\}}{}' Y_{i1}(\mathbf{R}_{i1}) Y_{12}(\mathbf{R}_{12}) \ldots Y_{nj}(\mathbf{R}_{nj}) \qquad (121)$$

can be written in terms of Fourier transforms:

$$S^{(xy)}_{i12\ldots nj}(\mathbf{R}_{ij}) = \left[\frac{\Delta}{(2\pi)^3}\right] \int_{\mathrm{BZ}} d\mathbf{t} \exp\left[i\mathbf{t} \cdot (\mathbf{R}_{lm} + \boldsymbol{\lambda}^{(xy)}_{ij})\right] \times \left(\sum_{\mathbf{p}} \phi^{(xa)}_{i1}(\mathbf{t}) \phi^{(ab)}_{12}(\mathbf{t}) \ldots \phi^{(pa)}_{nj}(\mathbf{t})\right) \qquad (122)$$

$\mathbf{p}$ denotes the set of symbols $a, b, \ldots, p$ which specify the positions of defects $1, 2, \ldots, n$ respectively in their unit cells. The convolution theorem may be used to establish the Fourier transform of a summation over a cycle of functions. The cycle sum defined as

$$S_{i12\ldots nj}(0) = (1/B) \sum_{\{\mathbf{n}+i+j\}} Y_{i1}(\mathbf{R}_{i1}) Y_{12}(\mathbf{R}_{12}) \ldots Y_{nj}(\mathbf{R}_{nj}) Y_{ji}(\mathbf{R}_{ji}) \qquad (123)$$

can be shown to be

$$S_{i12\ldots nj}(0) = \left(\frac{B_\Delta \Delta}{B(2\pi)^3}\right) \int_{\mathrm{BZ}} d\mathbf{t} \sum_{\mathbf{p}+x+y} \phi^{(xa)}_{i1}(\mathbf{t}) \phi^{(ab)}_{12}(\mathbf{t}) \ldots \phi^{py}_{nj}(\mathbf{t}) \phi^{(yx)}_{ji}(\mathbf{t}) \qquad (124)$$

where B_Δ is the number of unit cells in the crystal.

After these preliminaries the contribution of the cycle diagrams can now be found. We define the Fourier transform of a q-bond by the equation

$$\omega^{(xy)}_{ij}(\mathbf{t}) = \sum_{m}{}' \exp\left[-i\mathbf{t} \cdot (\mathbf{R}_{lm} + \boldsymbol{\lambda}^{(xy)}_{ij})\right] \times \left\{-\lambda c_i z_i z_j q_{ij}(\mathbf{R}_{lm} + \boldsymbol{\lambda}^{(xy)}_{ij})\right\} \qquad (125)$$

With the aid of the last two equations, the contribution of cycle diagrams, Eq. (117), can now be written as

$$S^{(c)} = \sum_{\mathbf{n} \geqslant \mathbf{2}} \left(\frac{B_\Delta \Delta}{B(2\pi)^3}\right) \int_{\mathrm{BZ}} d\mathbf{t} \left[\sum{}'' \sum_{\mathbf{p}} \prod \omega^{(xy)}_{ij}(\mathbf{t})\right] \qquad (126)$$

The double-primed summation is over all distinguishable arrangements of a set of vertices of fixed composition, $\mathbf{n}$, in a

simple cycle, like vertices being indistinguishable. The additional summation over $\mathbf{p}$ is over all possible assignments of each of the $\mathbf{n}$ defects to its allowed positions in the unit cell.

Let the permitted sites of defects i and j in the unit cell be the positions labelled $a, b, c, \ldots$ and $f, g, h, \ldots$ respectively. The matrix $\omega_{ij}(\mathbf{t})$ is defined by the equation

$$\omega_{ij}(\mathbf{t}) = \begin{vmatrix} \omega_{ij}^{(af)} & \omega_{ij}^{(ag)} & \omega_{ij}^{(ah)} & \ldots \\ \omega_{ij}^{(bf)} & \omega_{ij}^{(bg)} & \omega_{ij}^{(bh)} & \ldots \\ \omega_{ij}^{(cf)} & \omega_{ij}^{(cg)} & \omega_{ij}^{(ch)} & \ldots \\ . & . & . & \\ . & . & . & \\ . & . & . & \end{vmatrix} \tag{127}$$

For a crystal with σ different kinds of defects, $\alpha, \beta, \ldots$, we define a matrix of $\sigma\sigma$ dimensions

$$\mathbf{\Omega}(\mathbf{t}) = \begin{vmatrix} \omega_{\alpha\alpha} & \omega_{\alpha\beta} \ldots \\ \omega_{\beta\alpha} & \omega_{\beta\beta} \ldots \\ . & . \\ . & . \\ . & . \end{vmatrix} \tag{128}$$

The trace of the matrix $\mathbf{\Omega}^n$, i.e. $\mathbf{\Omega}$ multiplied by itself n times, gives a sum of products, each composed of n ω_{ij}-functions. The terms correspond to all possible compositions such that $\sum_{s=1}^{\sigma} n_s = n$, and for each composition the terms present correspond to every assignment of defects to distinguishable sites arranged in a cycle, like defects being treated as indistinguishable. When the definition of ω_{ij} in terms of $\omega_{ij}^{(xy)}$ is substituted in the expansion of the trace of $\mathbf{\Omega}^n$, then every term in the previous expansion is replaced in the final expansion by a set of terms with the same subscripts. The set of terms corresponds to every possible combination of assignments of the defects appearing in the subscripts to their allowed positions in the unit cell. Equation (126) can therefore be written in the form

$$S^{(c)} = \sum_{n \geqslant 2} \left(\frac{B_\Delta \Delta}{B(2\pi)^3} \right) \int_{\mathrm{BZ}} d\mathbf{t} [\mathrm{Tr}(\mathbf{\Omega}^n(\mathbf{t}))]/2n \tag{129}$$

The factor two arises because for every pattern generated from $\mathbf{\Omega}^n$ there is also generated its mirror image; the factor n arises because in the present context the n sites in the cycle are not labelled and there are just n points which one can select as a starting point in labelling sites.

If $\theta_1, \theta_2, \ldots, \theta_a$ are the eigenvalues of $\mathbf{\Omega}$ then

$$S^{(c)} = \sum_{n \geqslant 2} \left(\frac{B_\Delta \Delta}{B(2\pi)^3} \right) \int_{\mathrm{BZ}} d\mathbf{t} \left\{ \sum_{i=1}^{a} \frac{\theta_i^n}{2n} \right\} \tag{130}$$

and

$$\frac{1}{\alpha_r} \frac{\partial S^{(c)}}{\partial c_s^r} = \frac{1}{2} \left(\frac{B_\Delta \Delta}{B^r(2\pi)^3} \right) \int_{\mathrm{BZ}} d\mathbf{t} \left\{ \sum_{i=1}^{a} \frac{\theta_i}{1 - \theta_i} \cdot \frac{\partial \theta_i}{\partial c_s^r} \right\} \tag{131}$$

a is the number of different sites in the unit cell occupied by the σ different defects.

The evaluation of the contribution of cycle diagrams to the activity coefficient is formally complete once the eigenvalues of $\mathbf{\Omega}$ have been found. Let us write the result explicitly in terms of the Fourier transforms for the important case of two defects α and β each of which is allowed to occupy a particular one of the two positions in the unit cell. In this simple system the labelling of positions in the unit cell by superscripts on Fourier transforms becomes redundant and can be omitted. The result is

$$\frac{1}{\alpha} \frac{\partial S^{(c)}}{\partial c_\alpha} = \frac{\kappa^4}{8c_\alpha} \left[\frac{\Delta}{(2\pi)^3} \right] \times \int_{\mathrm{BZ}} d\mathbf{t} \left\{ \frac{\Delta^2(l_{\alpha\alpha} + l_{\beta\beta}) l_{\alpha\alpha} - \Delta^2(l_{\alpha\alpha} l_{\beta\beta} - l_{\alpha\beta} l_{\beta\alpha})(2 - \kappa^2 \Delta l_{\alpha\alpha})/2}{1 + \kappa^2 \Delta (l_{\alpha\alpha} + l_{\beta\beta})/2 + \kappa^4 \Delta^2 (l_{\alpha\alpha} l_{\beta\beta} - l_{\alpha\beta} l_{\beta\alpha})/4} \right\} \tag{132}$$

where κ is the Debye–Hückel screening constant defined by

$$\kappa^2 = \lambda \left(\sum_{s=1}^{\sigma} c_s z_s^2 \right) / \Delta \tag{133}$$

and $l_{\alpha\beta}$ is the Fourier transform, defined as in Eq. (119), of the function $q_{\alpha\beta}$, defined in Eq. (114).

(3) *Summation over Chains*

The sum $S^{(R)}$ may be written as the sum of contributions from

the different prototype patterns and the patterns derived from them: thus

$$S^{(R)} = \sum_{\sigma_{\mathbf{m}}} S(\sigma_{\mathbf{m}}) \tag{134}$$

where the sum is over all prototype patterns. $S(\sigma_{\mathbf{m}})$ is the sum of all contributions of the prototype pattern $\sigma_{\mathbf{m}}$ and all patterns derived from it by replacing one or more q-bonds by a q-bond chain. The q-bond chains may be of every possible composition and length, and of every possible arrangement of vertices within a given chain. In the notation of the preceding sections, it follows that

$$S(\sigma_{\mathbf{m}}) = \sum_{\mathbf{n} \geqslant \mathbf{0}} \frac{\mathbf{c}^{\mathbf{n}+\mathbf{m}}}{(\mathbf{m}+\mathbf{n})!} \sum_{\{\mathbf{m}+\mathbf{n}\}} \frac{M(\sigma_{\mathbf{m}})}{B} \frac{(\mathbf{m}+\mathbf{n})!}{\mathbf{m}! \prod_{k=1}^{\nu} \mathbf{n}_k!} \times \sum_{\delta(\mathbf{n})} R(\sigma_{\mathbf{m}};\ \delta(\mathbf{n}_1), \ldots, \delta(\mathbf{n}_\nu)) \tag{135}$$

The summation over $\delta(\mathbf{n})$ denotes the summation over all possible arrangements of vertices in each of the q-bond chains, the composition of the chains being $\mathbf{n} = \mathbf{n}_1 + \mathbf{n}_2 + \ldots \mathbf{n}_\nu$. The factor $(\mathbf{m}+\mathbf{n})!/\mathbf{m}! \prod_{k=1}^{\nu} \mathbf{n}_k!$ is the number of ways of choosing the sets $\mathbf{m}$ and $\mathbf{n}_1, \mathbf{n}_2, \ldots, \mathbf{n}_\nu$ from the set $(\mathbf{m}+\mathbf{n})$. $M(\sigma_{\mathbf{m}})$ is the number of times the prototype $\sigma_{\mathbf{m}}$ occurs in the sum S. In chain number k like defects may be interchanged in $\mathbf{n}_k!$ ways. Equation (135) can therefore be written as

$$S(\sigma_{\mathbf{m}}) = \frac{\mathbf{c}^{\mathbf{m}}}{\mathbf{m}!} \sum_{\{\mathbf{m}\}} M(\sigma_{\mathbf{m}})\, T(\sigma_{\mathbf{m}}) \tag{136}$$

where

$$T(\sigma_{\mathbf{m}}) = \sum_{\mathbf{n} \geqslant \mathbf{0}} \mathbf{c}^{\mathbf{n}} \sum_{\{\mathbf{n}\}} \sum_{\delta(\mathbf{n})}'' R(\sigma_{\mathbf{m}};\ \delta(\mathbf{n}_1), \ldots, \delta(\mathbf{n}_\nu))/B \tag{137}$$

The double prime on the summation over $\delta(\mathbf{n})$ signifies that it is over every arrangement of vertices in each of the q-bond chains when only vertices corresponding to different defect species are distinguishable. The summation over $\mathbf{n}$ gives terms corresponding to every possible composition of each of the ν chains. To carry out the summations over $\mathbf{n}$ and $\delta(\mathbf{n})$ we again employ the properties of the Fourier transforms and of the matrix $\boldsymbol{\Omega}$.

For a particular pattern we can write

$$\sum_{\mathbf{n}} \sum_{\delta(\mathbf{n})} \sum_{\{\mathbf{n}\}}'' R(\sigma_{\mathbf{m}};\ \delta(\mathbf{n}_1), \ldots, \delta(\mathbf{n}_\nu))\mathbf{c}^{\mathbf{n}}$$

$$= k(\sigma_{\mathbf{m}}) \left(\prod_{i,j \subset \mathbf{m}} \left[\frac{(-\lambda z_i z_j)^{\nu_{ij}}}{\nu_{ij}!} \right] \right) \prod_{k=1}^{\nu} L(n_k;\ \mathbf{R}_{ij}) \tag{138}$$

Here $k(\sigma_{\mathbf{m}})$ denotes the product of k-bonds corresponding to the prototype pattern $\sigma_{\mathbf{m}}$. The multiplication denoted by $\prod_{i,j \subset \mathbf{m}}$ signifies a product of terms, one for every pair of directly connected vertices in the set $\mathbf{m}$ of the prototype pattern. ν_{ij} is the sum of ν_{ij}^0 and the total number of q-bond chains between vertices i and j. The quantity $L(n_k;\ \mathbf{R}_{ij})$ is the sum over every composition of a total of n_k vertices in chain number k, the ends of the chain being defects i and j of the set $\mathbf{m}$. A term of given composition in the summand is the sum over all configurations of the sum of the products of q-bonds which correspond to every arrangement of the n_k vertices within the chain, like vertices being treated as indistinguishable. To carry out the chain summations we therefore require the quantity defined by the equation

$$m_{ij}^{(xy)}(\mathbf{R}_{ij}) = \sum_{n_k \geq 0} L(n_k;\ \mathbf{R}_{ij}) \tag{139}$$

By considering the Fourier transform of this sum and again using the properties of $\mathbf{\Omega}^n$ which we considered in detail above, it is straightforward to show[4] that

$$m_{ij}^{(xy)}(\mathbf{R}_{ij}) = \left[\frac{\Delta}{(2\pi)^3} \right] \int_{\mathrm{BZ}} d\mathbf{t} \exp(i\mathbf{t} \cdot \mathbf{R}_{ij}) c_j^{-1} \left[\sum_{k=1}^{a} \frac{\theta_k}{1 - \theta_k} \frac{\partial \theta_k}{\partial \omega_{ij}^{(xy)}} \right] \tag{140}$$

For the simple two-defect system introduced in the preceding section it is found that

$$\sum_{k=1}^{2} \frac{\theta_k}{1 - \theta_k} \frac{\partial \theta_k}{\partial \omega_{\alpha\alpha}} = \frac{\omega_{\alpha\alpha} + \omega_{\alpha\beta}\omega_{\beta\alpha} - \omega_{\alpha\alpha}\omega_{\beta\beta}}{1 - (\omega_{\alpha\alpha} + \omega_{\beta\beta}) + \omega_{\alpha\alpha}\omega_{\beta\beta} - \omega_{\alpha\beta}\omega_{\beta\alpha}} \tag{141}$$

$$\sum_{k=1}^{2} \frac{\theta_k}{1 - \theta_k} \frac{\partial \theta_k}{\partial \omega_{\alpha\beta}} = \frac{\omega_{\alpha\beta}}{1 - (\omega_{\alpha\alpha} + \omega_{\beta\beta}) + \omega_{\alpha\alpha}\omega_{\beta\beta} - \omega_{\alpha\beta}\omega_{\beta\alpha}} \tag{142}$$

In terms of the chain sum m_{ij}, the sum $S^{(R)}$ is found from Eqs. (134) and (136)–(139) to assume a very simple form, which is

$$S^{(R)} = \sum_{\mathbf{m}\geqslant \mathbf{2}} \frac{\mathbf{c}^{\mathbf{m}}}{\mathbf{m}!} \sum_{\sigma_{\mathbf{m}}} \sum_{\{\mathbf{m}\}} M(\sigma_{\mathbf{m}}) T(\sigma_{\mathbf{m}}) \tag{143}$$

where

$$T(\sigma_{\mathbf{m}}) = k(\sigma_{\mathbf{m}}) \prod_{i,j\subset \mathbf{m}} \frac{(m_{ij})^{\nu_{ij}}}{\nu_{ij}! B} \tag{144}$$

The products $T(\sigma_{\mathbf{m}})$ can be represented by the same diagrams as the corresponding prototype patterns occurring in the original expansion for $S^{(R)}$. Now each full-line bond represents the function m_{ij} instead of $(-\lambda z_i z_j q_{ij})$, and each dotted line represents a k-bond as before. There are of course no m-bond chains. The symbol ν_{ij} now denotes the number of direct m-bonds between vertices i and j of the set $\mathbf{m}$.

In the preceding paragraphs of this section we have summed the terms arising from the partial expansion of the exponentials occurring in the coefficients of the powers of particle concentrations to obtain a series of multiple infinite sums, the terms of which are convergent. The terms in $S^{(R)}$ are of the same form as those in the Mayer solution theory, apart from replacement of integration by summation and the fact that m_{ij} differs from the solution value because of the discreteness of the lattice. The evaluation of m_{ij} is outlined in the next section. It is found that the asymptotic form is

$$m_{ij}(\mathbf{R}_{ij}) = -\lambda z_i z_j A_{ij}(\kappa) \exp\left[-\kappa R_{ij}\xi(\kappa)\right]/4\pi R_{ij} \tag{145}$$

where A and ξ are both functions of κ which approach unity in the limit $\kappa \to 0$ and also in the limit that the lattice constant approaches zero. To develop the theory in a completely systematic manner as regards classification of terms in order of concentration therefore becomes even more complex than in the solution theory. However, in the limit $\kappa \to 0$ the situation is quite simple. Corresponding to each term in the solution theory there is a term in the present theory, which however involves small corrections of higher order in the concentration because of the functions A and ξ. We must refer the reader to the papers by Mayer[58] and Friedman[23] for details of the classification of the diagrams in order of concentration in this limit. This is of course an important step in the method.

Meeron[60,62] first pointed out how the terms in $S^{(R)}$ in the solution theory can be arranged in a form much more compact than that above, which is of the form of a virial expansion in which the coefficients involve the Debye–Hückel potential of average force rather than the unscreened potential. Similar manipulations can be made in the present case, but we shall omit the details, which are very simple, and quote only the final result. It is found using Meeron's form of $S^{(R)}$ that the activity coefficient of defect number s can be written

$$-\log \gamma_s^r = \frac{1}{\alpha^r}\frac{\partial}{\partial c_s^r}\{S^{(c)} + (S^{(c)} - S^{(1)}) - S^{(2)} + \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\frac{c_i c_j(H_{ij}-1)}{2} + \sum_{\mathbf{n}\geqslant 3}\frac{\mathbf{c}^{\mathbf{n}}}{B\mathbf{n}!}\sum_{\{\mathbf{n}\}}\mathscr{R}(\mathbf{n})\} \tag{146}$$

In this equation $S^{(1)}$ and $S^{(2)}$ are defined by the equation

$$S^{(n)} = \sum_{i=1}^{\sigma}\sum_{j=1}^{\sigma}\frac{c_i c_j}{2B}\sum_{\{ij\}}\frac{(m_{ij})^n}{n!} \tag{147}$$

The function H_{ij} is defined by

$$H_{ij} = \frac{1}{B}\sum_{\{ij\}} X_{ij} \tag{148}$$

$$X_{ij} = \exp\left(-[F_{ij}^{(s)}/kT - m_{ij}]\right) - 1 \tag{149}$$

Let us define a function ψ_{ij} by the equation

$$\psi_{ij} = X_{ij} - m_{ij} \tag{150}$$

The function $\mathscr{R}(\mathbf{n})$ may then be defined as the sum of all possible products of m-bonds and ψ-bonds, defined in exactly the same way as $R(\mathbf{n})$ except that connections are through all possible combinations of ψ-bonds and isolated m-bonds. (ψ- and m-bonds represent the functions ψ_{ij} and m_{ij} respectively.)

The work of Mayer shows that in the limit $c \to 0$ the expression for $\log \gamma_s^r$ in which all terms in the sum over $\mathbf{n} \geqslant \mathbf{3}$ are omitted includes all the terms of order c log c or lower. As in the Mayer solution theory one would hope to build with these terms a low-concentration theory valid over a wider range than the Debye–Hückel limiting law, which is contained in the cycle terms alone. In the following section we review the detailed evaluation of these

terms and then compare their form with those of the Lidiard–Bjerrum analysis.

(4) *Calculation of Leading Terms in the Formal Expressions*

All the formal expressions involve the Fourier transform l_{ij} of the function $q_{ij} = 1/4\pi R_{ij}$. We consider the case where i and j are defects on one of the primitive cubic lattices. $\mathbf{R}_l$ denotes the vector from defect i at the origin to defect j in unit cell number l. Born and Bradburn[10a] have shown that for an infinite lattice we can write

$$l_{ij}(\mathbf{t}) = (4\pi)^{-1} \sum_l{}' (R_l)^{-1} \exp(-i\mathbf{t} \cdot \mathbf{R}_l) \tag{151}$$

$$= (4\pi)^{-1}\tau^{\frac{1}{2}}[S_A + S_B - 2] \tag{152}$$

where

$$S_A = \sum_l{}' [\exp(-i\mathbf{t} \cdot \mathbf{R}_l)\theta_{-\frac{1}{2}}(\tau R_l^2\pi)] \tag{153}$$

$$S_B = (\Delta\tau^{\frac{3}{2}})^{-1} \sum_l \theta_0[(2\pi\mathbf{b}_l + \mathbf{t})^2/4\pi\tau] \tag{154}$$

In this expression S_A is summed over the direct lattice, $\mathbf{R}_l$; S_B is summed over the reciprocal lattice, $\mathbf{b}_l$. The parameter τ is chosen so as to obtain equally rapid convergence in the sums over the direct and reciprocal lattices. The θ functions are defined by

$$\theta_0(x) = e^{-x}/x$$
$$\theta_{-\frac{1}{2}}(x) = (\pi/x)^{\frac{1}{2}}[1 - \Phi(x^{\frac{1}{2}})],$$

where $\Phi(x)$ is Gauss' error function, and have been tabulated by Misra[65] for the primitive cubic lattices. The value of $l_{ij}(\mathbf{t})$ in the limit $\mathbf{t} \to 0$ can be found by expanding exponential functions and retaining the leading terms. The result is

$$\Delta l_{ij}(\mathbf{t}) = \mathscr{B}_{ij} + 1/t^2 \tag{155}$$

where

$$\mathscr{B}_{ij} = (\Delta\tau^{\frac{1}{2}}/4\pi)[S_C + (S_D - 1)/(\Delta\tau^{\frac{3}{2}}) - 2]$$
$$S_C = \sum_l{}'\theta_{-\frac{1}{2}}(\tau R_l^2\pi)$$
$$S_D = \sum_l{}' \theta_0(\pi b_l^2/\tau)$$

The structure-dependent coefficients have been calculated for the three primitive cubic lattices.[4] For the sodium chloride lattice we have $\Delta = 2a^3$, where a denotes the anion–cation lattice spacing, and if we define a parameter b_{ij} by the equation

$$\mathscr{B}_{ij} = -a^2 b_{ij} \tag{156}$$

then the numerical values are found to be[4]

$$b_{++} = b_{--} = 0.36485; \qquad b_{+-} = b_{-+} = 0.08673 \tag{157}$$

where the subscripts + and − refer to defects on the cation and anion sublattices respectively. Note that in the limit that the lattice spacing goes to zero the transform in Eq. (155) reduces to the value t^{-2} used in the Mayer solution theory. The terms of next highest order in t in Eq. (151) for l_{ij} lead to expressions too complex to be of value. However, as long as we are interested in long-range effects, which lead to Debye–Hückel results in the continuum limit, the asymptotic expression in the limit $\mathbf{t} \to 0$ should prove sufficient. In this section we restrict consideration to the case of Schottky defects in a sodium chloride lattice or to equal numbers of divalent cations and cation vacancies in the same lattice. For both systems we have

$$\begin{aligned} l_{\alpha\beta} &= l_{\beta\alpha}, \qquad l_{\alpha\alpha} = l_{\beta\beta} \\ |z_\alpha| &= |z_\beta| = 1, \qquad c_\alpha = c_\beta = c \end{aligned} \tag{158}$$

Let us first consider the evaluation of the activity coefficient apart from the final set of terms corresponding to diagrams with three or more vertices (Eq. (146)).

The contribution of the cycle diagrams can be found from Eq. (132) using the asymptotic form for the Fourier transforms (Eq. (155)) and is

$$\frac{1}{\alpha}\frac{\partial S^{(c)}}{\partial c_\alpha} = \frac{\kappa^4 \Delta}{4c_\alpha (2\pi)^3} \int_{\mathrm{BZ}} d\mathbf{t} \{\mathscr{F}/t^2 + \mathscr{E} + \mathscr{G}t^2\}/(t^2 + \kappa^2 \xi^2) \tag{159}$$

where

$$\xi^2 = [1 + \kappa^2(\mathscr{B}_{\alpha\alpha} - \mathscr{B}_{\alpha\beta})/2]/[1 + \kappa^2 \mathscr{B}_{\alpha\alpha} + \kappa^4(\mathscr{B}_{\alpha\alpha}^2 - \mathscr{B}_{\alpha\beta}^2)/4]$$

and

$$\mathscr{E} = [4\mathscr{B}_{\alpha\beta} - 2\mathscr{B}_{\alpha\alpha} + \kappa^2(3\mathscr{B}_{\alpha\alpha}^2 - \mathscr{B}_{\alpha\beta}^2 - 2\mathscr{B}_{\alpha\alpha}\mathscr{B}_{\alpha\beta})]/ [1 + \kappa^2 \mathscr{B}_{\alpha\alpha} + \kappa^4(\mathscr{B}_{\alpha\alpha}^2 - \mathscr{B}_{\alpha\beta}^2)/4]$$

$$\mathscr{F} = [1 + 2\kappa^2(\mathscr{B}_{\alpha\alpha} - \mathscr{B}_{\alpha\beta})]/[1 + \kappa^2\mathscr{B}_{\alpha\alpha} + \kappa^4(\mathscr{B}^2_{\alpha\alpha} - \mathscr{B}^2_{\alpha\beta})/4]$$
$$\mathscr{G} = [2\mathscr{B}^2_{\alpha\beta} - \mathscr{B}^2_{\beta\beta} + \kappa^2\mathscr{B}_{\alpha\alpha}(\mathscr{B}^2_{\alpha\alpha} - \mathscr{B}^2_{\alpha\beta})]/$$
$$[1 + \kappa^2\mathscr{B}_{\alpha\alpha} + \kappa^4(\mathscr{B}^2_{\alpha\alpha} - \mathscr{B}^2_{\alpha\beta})/4]$$

In the limit that the lattice spacing goes to zero then

$$\xi, \mathscr{F} \to 1; \qquad \mathscr{E}, \mathscr{G} \to 0$$

and the range of integration extends over the whole of reciprocal space. The contribution of the cycle diagrams then reduces to the corresponding solution theory value,

$$\frac{1}{\alpha}\frac{\partial S^{(c)}}{\partial c_\alpha} = \frac{\Delta\kappa^3}{16\pi c_\alpha} = \frac{1}{2}\left(\frac{z_\alpha^2 e^2}{DkT}\right)\kappa \tag{160}$$

The remaining terms in the expression for the activity coefficient all involve the function m_{ij} defined in Eq. (140). Using the asymptotic expression for the Fourier transform in Eq. (155) it is found that

$$m_{\alpha\beta}(\mathbf{R}_{\alpha\beta}) = -\lambda z_\alpha z_\beta \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{t}\, \exp[i\mathbf{t}\cdot\mathbf{R}_{\alpha\beta}]$$
$$\times\left(\frac{\mathscr{D}(1 - \mathscr{B}_{\alpha\beta}\kappa^2\xi^2)}{t^2 + \kappa^2\xi^2} + \mathscr{D}\mathscr{B}_{\alpha\beta}\right) \tag{161}$$

where $\alpha \neq \beta$, and

$$m_{\alpha\alpha}(\mathbf{R}_{\alpha\alpha}) = -\lambda z_\alpha^2 \frac{1}{(2\pi)^3}\int_{\mathrm{BZ}} d\mathbf{t}\, \exp[i\mathbf{t}\cdot\mathbf{R}_{\alpha\alpha}]\left(\frac{\mathscr{A} - \kappa^2\xi^2}{t^2 + \kappa^2\xi^2} + \mathscr{T}\right) \tag{162}$$

The following abbreviations were used

$$\mathscr{D} = 1/[1 + \kappa^2\mathscr{B}_{\alpha\alpha} + \kappa^4(\mathscr{B}^2_{\alpha\alpha} - \mathscr{B}^2_{\alpha\beta})/4]$$
$$\mathscr{A} = [1 + \kappa^2(\mathscr{B}_{\alpha\alpha} - \mathscr{B}_{\alpha\beta})]\mathscr{D}$$
$$\mathscr{T} = [\mathscr{B}_{\alpha\alpha} + \kappa^2(\mathscr{B}^2_{\alpha\alpha} - \mathscr{B}^2_{\alpha\beta})/2]\mathscr{D} \tag{163}$$

In the limit that the integral can be extended over all reciprocal space the expression reduces to

$$m_{\alpha\beta}(\mathbf{R}_{\alpha\beta}) = -\lambda z_\alpha z_\beta A_{\alpha\beta} \exp(-\kappa\xi R_{\alpha\beta})/4\pi R_{\alpha\beta} \tag{164}$$

where

$$A_{\alpha\beta} = \mathscr{D}(1 - \mathscr{B}_{\alpha\beta}\kappa^2\xi^2), \qquad \alpha \neq \beta$$
$$A_{\alpha\alpha} = \mathscr{A} - \mathscr{T}\kappa^2\xi^2$$

for $\mathbf{R}_{\alpha\beta} \neq 0$.

Once the value of $m_{\alpha\beta}$ has been established, the evaluation of the remaining terms in Eq. (150) for the activity coefficient follows quite simply. The fourth term on the right-hand side clearly involves interactions of oppositely charged defects of the sort considered in the Lidiard–Bjerrum theory. It can be written for the systems under consideration as

$$\begin{aligned}\frac{1}{\alpha}\frac{\partial}{\partial c_\alpha}\{\sum_i\sum_j c_i c_j(H_{ij}-1)/2\} \\ = c\{\sum_{\{\alpha\}}'(\exp[m_{\alpha\alpha}-F_{\alpha\alpha}^{(s)}/kT](1+\kappa A_{\alpha\alpha}be^{-\kappa\xi R_{\alpha\alpha}}/4)-1) \\ +\sum_{\{\beta\}}'(\exp[m_{\alpha\beta}-F_{\alpha\beta}^{(s)}/kT](1-\kappa A_{\alpha\beta}be^{-\kappa\xi R_{\alpha\beta}}/4)-1)-2\}\end{aligned} \tag{165}$$

where

$$b = e^2/DkT$$

The only satisfactory procedure for evaluating this contribution is by direct summation for small separations and numerical integration for the remainder (see Ref. 4).

The second term on the right-hand side of Eq. (146) vanishes in the continuum limit when use is made of electrical neutrality. For the defects in the impure crystal the term is again zero. In the intrinsic case it is not identically zero but is much smaller than the other terms (details can be found in Ref. 4). The final term to be evaluated in Eq. (146) is found, by substituting the asymptotic value of m_{ij}, to be

$$\frac{1}{\alpha}\frac{\partial S^{(2)}}{\partial c_\alpha} = \frac{\kappa^4\Delta^2}{128\pi^2 c}\sum_{j=\alpha,\beta}A_{\alpha j}^2\{\sum_{\{j\}}'e^{-2\kappa R_{\alpha j}\xi}(1/R_{\alpha j}-\kappa\xi/2)/R_{\alpha j}\} \tag{166}$$

where terms arising from the concentration dependence of A_{ij} and ξ have been neglected. In the continuum limit $A_{ij}\to 1$ and the summation may be replaced by integration. This then reduces correctly to

$$\frac{1}{\alpha}\frac{\partial S^{(2)}}{\partial c_\alpha} = \frac{3}{16}\left(\frac{z_\alpha^2 e^2}{DkT}\right)\kappa \tag{167}$$

In numerical work quoted below the summations in Eq. (166) were treated in the same way as those in Eq. (165) and appreciable differences from the continuum limit value were found.[4]

Some numerical results have been obtained for Schottky defects in sodium chloride and for cation vacancies in sodium chloride doped with manganese chloride so that the number of intrinsic defects is negligible. Figure 9 shows the results for the

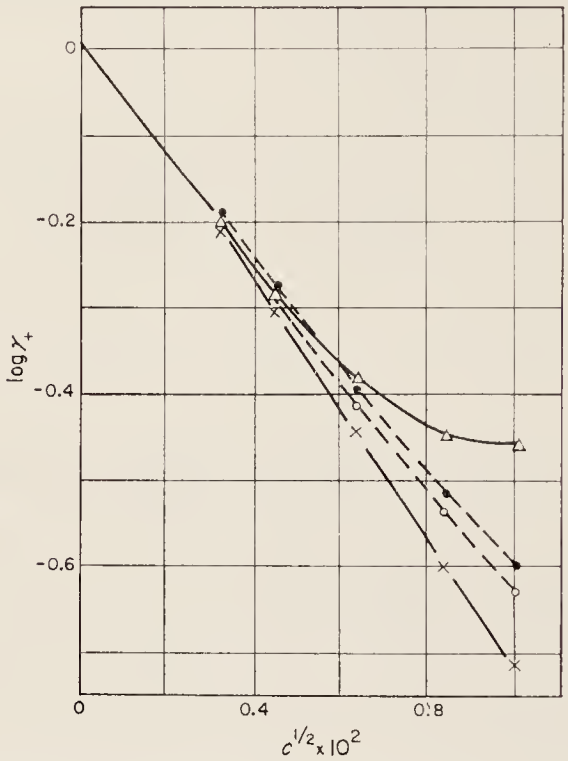

Fig. 9. Logarithm of the cation activity coefficient versus the square root of the concentration for the system of manganese ions and cation vacancies in sodium chloride at 500°C. Filled-in circles represent the association theory with $R_q = 2a$, and open circles the association theory with $R_q = b/2$. Crosses represent the present theory with cycle diagrams plus diagrams of two vertices, and triangles represent the same but with triangle diagram contributions added.

doped crystal at 500°C. The crosses show the results calculated for the approximation of cycle diagrams plus diagrams with two vertices (i.e. from Eqs. (146), (160), and (165)–(166)). For the contribution of cycle diagrams the formula for the continuum limit was used because the error involved is negligible over the concentration range of interest. The functions A and ξ were found to differ very little from unity in the same range. (A

detailed breakdown of the numerical contributions to the activity coefficient, the values of A and ξ at 400°, 500°, and 600°C, and some results for the pure crystal can be found in Ref. 4.) In order to try and check the rate of convergence of the complete expansion, the contributions of diagrams containing three vertices to the activity coefficient were also estimated, with rather lower accuracy. When these contributions are included the curve indicated by triangles is obtained. From the values calculated in this manner it was concluded that at temperatures as low as 400°C convergence of the expansion is too slow for the formalism to be of practical value. Even at 500°C the range is limited to a concentration of 10^{-4} or below. Although the highest concentration at which the theory can be used increases with increasing temperature, the range of practical usefulness for doped crystals is not much increased at 600°C as compared with 500°C, since the concentration of intrinsic defects is approximately 8×10^{-6} at the higher temperature.

The following remarks should be made. The contributions from three-vertex diagrams come mainly from configurations in which at least two of the "bonded" defects of the diagram are nearest or next nearest neighbours. It may be that triplet forces, $F^{(3)}$, are not negligible at just those configurations which are making much the greatest contribution. Finally, it would be of interest to try and define more closely than has so far been attempted the conditions under which higher powers in t become important in the expansion l_{ij} (Eq. (151)), and under which the extension of the range of integration from the edge of the Brillouin zone to infinity becomes inadmissible, in evaluating m_{ij}. These points are now being studied. However, we do not believe these refinements would influence our conclusions about the slow convergence of the series expansion very much.

C. Distribution Functions

The discussion of the defect distribution functions and potentials of average force follows along rather similar lines to that for the activity coefficient. The formal cluster expansions, Eqs. (90)–(91), individual terms of which diverge, must be transformed into another series of closed terms. This can clearly be done by

exactly the same technique of diagram classification followed by summation over chains using the Fourier transform technique. Since the method introduces nothing that is new we shall merely quote the final result for the pair correlation function. The

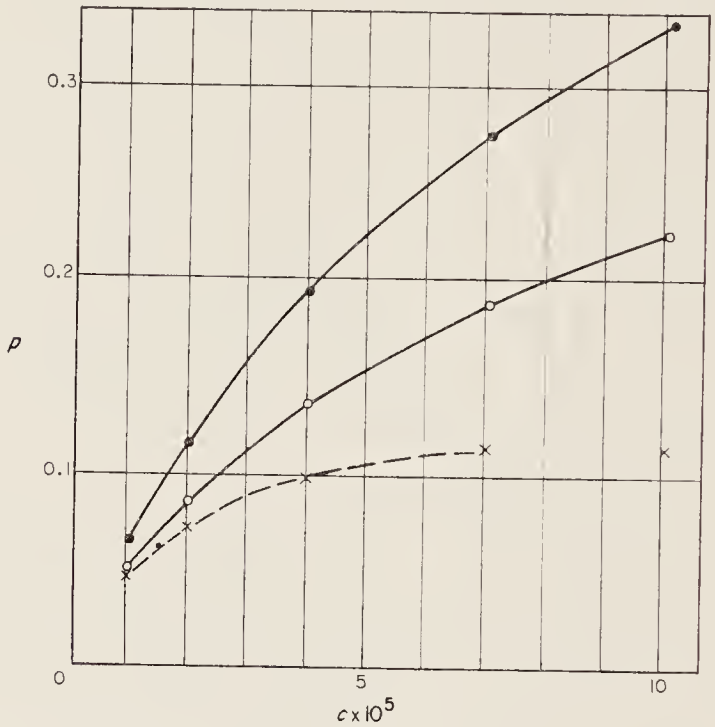

Fig. 10. The degree of association into nearest- and next-nearest-neighbour complexes, p, versus concentration, c, at 500°C for manganese ions and cation vacancies in sodium chloride. Filled circles represent the simple association theory, open circles the Lidiard association theory, and crosses the present theory using Eq. (173) when the first term only has been retained in the virial appearing in the equation for the defect distribution function (Eq. (168)). The point of highest concentration represented by a cross may be in error due to the neglect of higher terms in the virial series, and the dotted curve has not been extended to include it.

corresponding solution theory problem has been discussed by Meeron[62] and the discussion for defects follows a similar pattern apart from the complications due to the discreteness of the lattice. For the pair correlation function it is found that

$$g(\{ij\}) = \exp\left(m_{ij}(\mathbf{R}_{ij}) - F^{(s)}/kT\right)\left[1 + \sum_{\mathbf{m}\geqslant\mathbf{1}} \frac{\mathbf{c}^{\mathbf{m}}}{\mathbf{m}!} \sum_{\{\mathbf{m}\}} \eta(ij:\mathbf{m})\right] \quad (168)$$

Here the function $\eta(ij:\mathbf{m})$ is defined exactly as for $P(ij;\ \mathbf{m})$ except that connections are now through all possible combinations of ψ-bonds and isolated m-bonds.

Meeron[62] has studied the order with respect to c of the terms in the corresponding solution theory equations. Numerical estimates of g have been made for the same doped sodium chloride system as that discussed for activity coefficients. Only the first term in the expansion above was retained and the lattice summation was done numerically. m_{ij} was calculated using Eq. (164). The magnitude of the first term in the expansion for g increases rapidly with concentration and the convergence properties of the expansion are believed to be rather similar to those of the activity coefficient expansion. The distribution function was used to calculate the degree of association of manganese ions and cation vacancies to form nearest-neighbour complexes and to form next-nearest-neighbour complexes using Eq. (173). Figure 10 shows the results for nearest-neighbour complexes at 500°C and the corresponding prediction from the Lidiard–Bjerrum theory (Eq. (106)). Let us now consider briefly the basis of this last calculation.

D. Association in Terms of Defect Distribution Functions

As already remarked (Section VI-A) the properties of complexes of nearest-neighbour cation–vacancy-divalent cation pairs are very important for the interpretation of experimental data on ionic crystals. Lidiard's[51] modification of the Bjerrum ionic association theory to the solid state, which proceeds by use of the law of mass action, is employed. The more fundamental formulation of the Bjerrum association theory in terms of the associated particles has been considered by Fuoss[27] and more recently by Poirier and DeLap,[70] who corrected and extended the earlier treatment. Allnatt and Cohen[4] have recently given a similar treatment for the case of two kinds of lattice defects, α and β, carrying opposite charges. More complex systems involving larger numbers of different kinds of defects have not so far been of much practical importance in ionic crystals, but a very general formulation to cover the various possibilities would be more

difficult than the corresponding ionic solution theory. Let us outline the formulation and add some additional remarks.

We define an "i-th nearest neighbour complex" to be a pair of oppositely charged defects on lattice sites which are i-th nearest neighbours, such that neither of the defects has another defect of opposite charge at the i-th nearest neighbour distance, R_i, or closer. This corresponds to what is called the "unlike partners only" definition. A different definition is that the defects be R_i apart and that neither of them has another defect of *either* charge at a distance less than or equal to R_i. This is the "like and unlike partners" definition. For ionic defects the difference is small at the lowest concentrations; the definition to be used depends to some extent on the problem at hand. We shall consider only the first definition. It is required to find the concentration of such complexes in terms of the defect distribution functions. It should be clear that what is required is merely a particular case of the "specialized distribution functions" of Section IV-D and that the answer involves pair, triplet, and higher correlation functions. In fact this is not the procedure usually employed, as we shall now see.

The probability of finding a defect of type α at a prescribed lattice site together with a defect of type β on any lattice site which is at a distance R_i from α is

$$\sum_{(|R_{\alpha\beta}|=R_i)} \rho^{(2)}(\{\alpha\beta\}_i) = c_\alpha c_\beta g(\{\alpha\beta\}_i)\phi_i(\alpha\beta) \tag{169}$$

(The notation introduced at the beginning of Section V is employed.)

The quantity $G(\{\alpha\beta\}_i)$ is defined as the probability of finding a defect of type β on a site a distance R_i from a particular α defect so that they constitute an "i-th nearest neighbour complex" ("unlike partners only" definition). Let $E(t;\ R_i)$ be the probability that a defect of type t does not have a defect partner at a distance less than or equal to R_i except on one site at a distance R_i. From the definitions made it follows that

$$G(\{\alpha\beta\}_i) = E(\alpha;\ R_i)E(\beta;\ R_i)c_\beta g(\{\alpha\beta\}_i)\phi_i(\alpha\beta) \tag{170}$$

$$c_\alpha G(\{\alpha\beta\}_i)\phi_i(\beta\alpha) = c_\beta G(\{\beta\alpha\}_i)\phi_i(\alpha\beta) \tag{171}$$

The exclusion factor $E(\alpha;\ R_i)$ is, from its definition,

$$E(\alpha;\ R_i) = 1 - \sum_{j=1}^{i} G(\{\alpha\beta\}_i)\ [(\phi_i(\alpha\beta) - \delta_{ij})/\phi_i(\alpha\beta)] \qquad (172)$$

where terms of the order of $1/N$ have been omitted in the summation.[27,70] The term in square brackets arises from the fact that one of the sites a distance R_i from α must be excluded since it will be occupied by the partner of α. The equations (170)–(172) correspond to the set of coupled integral equations for $G(\{\alpha\beta\}_i)$ of ionic solution theory. However, further development in a general manner is more difficult to achieve in the present case. From these equations the equation for $E(\alpha;\ R_1)$ is found by straightforward manipulations to be[4]

$$\begin{aligned}[E(\alpha;\ R_1)]^2 c_\alpha g(\{\alpha\beta\}_1)[\phi_1(\beta\alpha) - 1] \\ - E(\alpha;\ R_1)\{c_\alpha g(\{\alpha\beta\}_1)[\phi_1(\beta\alpha) - 1] \\ - c_\beta g(\{\alpha\beta\}_1)[\phi_1(\alpha\beta) - 1] - 1\} = 1\end{aligned} \qquad (173)$$

and hence $G(\{\beta\alpha\}_1)$ can be found from Eq. (172). Other values of $E(\alpha;\ R_i)$ for $i > 1$, and hence values of $G(\{\beta\alpha\}_i)$, can be found from a recurrence relation between $E(\alpha;\ R_{i+1})$ and $E(\alpha;\ R_i)$ which is readily derived and is given in Ref. 4.

The probability that a defect of type α has a partner in a complex at a separation less than or equal to R_q is

$$p_{\alpha\beta} = \sum_{i=1}^{q} G(\{\alpha\beta\}_i) \qquad (174)$$

Let us restrict further discussion to the case of equal and opposite charges on a sodium chloride lattice and use the definitions

$$\begin{aligned} c &= c_\alpha = c_\beta \\ \phi_i &= \phi_i(\alpha\beta) = \phi_i(\beta\alpha) \\ p &= p_{\alpha\beta} = p_{\beta\alpha} \end{aligned} \qquad (175)$$

In the terminology of association theory p is the degree of association into complexes which have been defined to include "excited states" up to a separation of q-th nearest neighbours (cf. Section VI-A). The result for nearest-neighbour association in the limit of zero concentration is similar to, but not quite identical with,

that of the "simple association theory" (i.e. Eq. (106) with $\gamma_D = 1$). From Eqs. (170) and (172), we have

$$p = \phi_1 c g(\{\alpha\beta\}_1)[1 - p(1 - 1/\phi_1)]^2 \tag{176}$$

In the limit of zero concentration $\phi_1 g(\{\alpha\beta\}_1)$ becomes equal to the equilibrium constant K_2 of Eq. (106) and hence

$$K_2 = p/[1 - p(1 - 1/\phi_1)]^2 c \tag{177}$$

Each factor in square brackets arises from an exclusion factor, E, in the defining equation for the distribution function G, Eq. (170). The factor $(1 - 1/\phi_1)$ by which the result differs from the simple association theory arises from the term in square brackets in Eq. (172) and has already been commented on.

The result for the "like and unlike partners" definition can be obtained by very similar arguments and involves all three pair correlation functions. The various definitions and results can equally be applied to defects which are not ionic by merely substituting the words "different kind" for "opposite charge" and "either kind" for "either charge" in the definitions.

It remains to comment on the fact that, contrary to expectation, the integral relation for G involves only $g^{(2)}$ and no higher correlation functions. This arises because in writing Eq. (172) the implicit assumption is made that the probability of finding a second partner, say β', to a given defect, α, is the same as it would be if the defect α did not already have a partner β. In fact $g^{(3)}(\{\alpha\beta\beta'\})$ has been replaced by $g^{(2)}(\{\alpha\beta'\})$. This is even stronger than the Kirkwood superposition approximation[33]

$$g^{(3)}(\{\alpha\beta\beta'\}) = g^{(2)}(\{\alpha\beta\})g^{(2)}(\{\alpha\beta'\})g^{(2)}(\{\beta\beta'\}) \tag{178}$$

The formula for specialized distribution functions makes no such assumptions and hence involves $g^{(3)}$. It also involves $g^{(4)}, g^{(5)}, \ldots$ since correction is made for the possibility of a defect having two, three, . . . other partners simultaneously. Using Eq. (171) and the superposition approximation one finds that for the sodium chloride type lattice

$$\begin{aligned} p &= \sum_{(|\mathbf{R}_{\alpha\beta}| = R_1)} \rho^{(2)}(\{\alpha\beta\}_1;\ \mathbf{B} - \mathbf{b})/c_\alpha \\ &= \phi_1 c g^{(2)}(\{\alpha\beta\}_1)[1 - c \sum_{\{\beta'\}}^{(b=\alpha 1)} g^{(2)}(\{\alpha\beta^1\})g^{(2)}(\{\beta\beta'\}) \\ &\qquad - c \sum_{\{\alpha^1\}}^{(b=\beta 1)} g^{(2)}(\{\alpha\alpha^1\})g^{(2)}(\{\beta\alpha^1\}) + O(c^2)] \end{aligned} \tag{179}$$

where the restriction ($b = \alpha 1$) means that the summation is restricted to sites which are first neighbours to defect α. If the interaction between the first and second partners is neglected in the manner of the association theory given by Allnatt and Cohen then

$$p = \phi_1 c g^{(2)}(\{\alpha\beta\}_1)\{1 - 2c(\phi_1 - 1)g(\{\alpha\beta\}_1) + \ldots\}$$

which is the same as solving the association theory expression for p (Eq. (176)) to the same order in c, as would be expected. It is evident that attempts to go beyond the "simple association theory" or the more elaborate equations of Allnatt and Cohen require a more detailed knowledge of the defect distribution functions than is generally available.

E. Discussion

In this section we comment briefly on the results obtained above, the relation of the formalism to that used by Lidiard[53] and other workers, and possible further developments. The calculation of the triangle diagram contributions to the activity coefficient for the impure crystal shows clearly that at temperatures much below 500°C the expansion converges too slowly to be of value at any concentration of interest, while at 500°C the inclusion of the triangle contribution is quite necessary to obtain results up to a concentration of 10×10^{-5} mole fractions of impurity. (This may be compared with the concentration range in the conductivity measurements of Etzel and Maurer of $1\text{–}70 \times 10^{-5}$ mole fractions. Lower concentrations may be used in dielectric loss and paramagnetic resonance studies although these are generally made at lower temperatures; for example, a typical concentration in Watkins'[86] experiments was 6×10^{-5}.) This is a small range compared with that obtained using the Mayer ionic solution theory. For 1:1 electrolytes in aqueous solution at 25°C the corresponding terms, but without triangle diagram contributions, suffice to fit the experimental results up to a mole fraction of solute of approximately 700×10^{-5}. The reason is, of course, the difference in dielectric constant. A more reasonable comparison can be made by noting that apart from the lattice constant (or the distance of closest approach in the solution theory), the

parameter on which terms such as that in Eq. (165) depend is $\tau = \kappa b/2$, which is the contribution of the cycle diagrams to $\log \gamma$. The largest value of τ at which the contribution of cycle diagrams plus that of diagrams involving two vertices, i.e. terms corresponding to the Debye–Hückel limiting law plus the contribution of the "ion pairs" of the Bjerrum theory, is sufficient in the solution theory is 0.74.[69] Allowing for differences due to the use of lattice summation instead of integration in evaluating some of the terms in $\log \gamma$, the behaviour is found to be comparable.

It is shown below that use of the present formalism, without triangle terms or higher contributions, is essentially equivalent to using the Lidiard–Bjerrum type of theory. The latter appears to be an approximation to the former in a first approximation valid only at very low concentrations. The fact that these terms are only first members of an expansion which converges very slowly in the range of temperatures and concentrations of experimental interest emphasizes once more the doubtful validity of using the Lidiard association theory for the calculation of the activity coefficients of defects at high doping concentrations. (For example, at 400°C configurations which involve three defects and are not included in the Lidiard theory make an appreciable contribution even at concentrations as low as 2×10^{-5}. At higher concentrations configurations involving still more defects would have to be considered.)

A comparison between the present results and the association theory for activity coefficients is made in Fig. 9. The association-theory activity coefficient is $(1 - p)\gamma_D$, where p and γ_D are to be calculated from Eqs. (106) and (107). As is well known, the results are not sensitive to the choice of the distance R_q defining the associated pairs. Dashed lines in the figure show the results for the Bjerrum distance ($R_q = e^2/2DkT$) and for the case when only neighbours with non-Coulombic interactions (i.e. nearest and next-nearest neighbours) are treated as associated. Above $c = 7 \times 10^{-5}$ the triangle diagrams become increasingly important and the association theory gives results between the values calculated with and without such contributions. However, even at the highest concentration on the graph, and certainly at much higher concentrations, diagrams with a greater number of vertices would have to be calculated to make a convincing calculation of

log γ, so that a check on the predictions of the association theory is not possible.

Similar considerations apply to the calculation of the degree of association. At low concentrations and sufficiently high temperatures, our results for the degree of association show that the Lidiard theory underestimates the decrease in degree of association due to the long-range Coulomb forces, although it is of course much better than the simple association theory which neglects them entirely (Fig. 10). However, at concentrations higher than those in Fig. 10 terms of higher order in the virial expansion will make appreciable contributions, but their calculation would be so time-consuming as to be impracticable. We are therefore not in a position to estimate the accuracy of the Lidiard theory at high doping levels, in particular at lower temperatures where the degree of association approaches unity. In these circumstances the Lidiard theory appears to correspond to retention of only the leading terms of a slowly convergent series.

The problem, apart from differences due to the discreteness of the lattice, is essentially similar to that in the electrochemistry of solutions of low dielectric constant, a field for which adequate theories are not yet available. However, certain possibilities are opened up by using the cluster method and focussing attention on the radial distribution functions. It has recently been shown[2a] that the Mayer–Meeron ionic solution cluster expansions can be expressed as a set of integral equations for the radial distribution functions. Numerical solution of this equation by iteration offers a convenient means of calculating the distribution functions from the contributions of whole classes (composed of infinite series) of the diagrams in the cluster expansions and should be more efficient than calculating individual diagrams in the manner used here. The method is a slight variant of the nodal expansion method of Meeron[63] and others.[47] Since no numerical results are yet available we shall not discuss the method further. (For Coulomb systems only the dilute electron gas has been studied numerically by Meeron's method.[14]) Accurate distribution functions would be extremely valuable in the interpretation of transport properties.[2b] Indeed, measurements of equilibrium properties of ionic crystals of sufficient detail or precision to warrant a detailed comparison between experiment and theory are not available, and the ultimate

test of equilibrium theories, even if eventually available over a wider range of conditions, will involve non-equilibrium measurements. So far the association theory of Eq. (106) has been used. It is interesting to note that this equation is used both in the calculation of activity coefficients and of defect distribution functions, whereas these calculations are separated in the present formalism. This will be clear from the following paragraph, which serves to point out the connection between the Lidiard–Bjerrum formalism and that of Mayer.

We consider first the activity coefficients. The contribution of the defects, N cation vacancies and N divalent ions, to the Gibbs free energy of the doped crystal is

$$G = N\bar{\mu}_1 + N\bar{\mu}_2 \tag{180}$$

where $\bar{\mu}_1$ and $\bar{\mu}_2$ are the corresponding defect "chemical potentials" defined in Section IV-B, and the corresponding activity coefficients γ_1 and γ_2 can be calculated by the methods described. In the association theory the same free energy is ascribed to N' "free" vacancies, N' "free" impurity ions, and N_k "complexes". If p is the degree of association then $N' = (1 - p)N$, and formulating the association theory in terms of chemical potentials[6] we have

$$G = N(1 - p)\mu_1 + N(1 - p)\mu_2 + Np\mu_3 \tag{181}$$

where μ_1, μ_2, μ_3 are the chemical potentials for "free" vacancies, "free" impurity ions, and complexes. The activity coefficients of the "free" vacancies and of the impurity ions are taken as the Debye–Hückel value, γ_D (Eqs. (107) and (108)), and the activity coefficient of the complexes as unity. It can be shown[75] using the condition for equilibrium between the three types of defects,

$$\mu_3 = \mu_1 + \mu_2 \tag{182}$$

and the fact that $\gamma_1 = \gamma_2$, that Eqs. (180) and (181) are equivalent provided that

$$\gamma_1 = (1 - p)\gamma_D \tag{183}$$

For simplicity we consider only the continuum limit (i.e. Mayer ionic solution theory). The last equation allows us to calculate the value of p which the association theory should predict in order to be compatible with the true value, which we assume to be given by the Mayer theory in the range considered. It is

straightforward to show that the Mayer activity coefficient (omitting diagrams with three or more vertices) can be written

$$-\log \gamma_1 = \tau - \tau^2 + c \int_a^{R_q} e^{be^{-\kappa R}/R}(1 - \kappa be^{-\kappa R}/4)d\mathbf{R} + c \int_a^{R_q} e^{-be^{-\kappa R}/R}(1 + \kappa be^{-\kappa R}/4)d\mathbf{R} \quad (184)$$

where terms of higher order than $\tau^2(c)$ have been neglected. $R_q = b/2$ is the Bjerrum distance (Section VI-A) and all distances of closest approach are taken to be equal to a. The last term is negligible at low concentrations so that from Eqs. (107), (183), and (184)

$$-\log (1 - p) = c \int_a^{R_q} e^{be^{-\kappa R}/R}(1 - \kappa be^{-\kappa R}/4)d\mathbf{R}$$

At concentrations at which the neglect of the higher terms is justified $-\log (1 - p) \approx p$ and at infinite dilution we have

$$p/c\gamma_D^2 = \int_a^{R_q} e^{b/R}d\mathbf{R} \quad (185)$$

which is just the Bjerrum result. At finite concentrations it is clear that the value of p predicted from the Bjerrum formula will not be the same as that calculated from Eq. (183) and the activity coefficient will differ from that predicted by the Mayer theory retaining cycle diagrams and diagrams with two vertices (cf. Fig. 9).

It can also be seen that the value of p calculated from Eq. (183) will not be identical with the degree of association defined in terms of distribution functions except at infinite dilution. In the continuum limit we have[70]

$$p = c \int_a^{R_q} g(R)4\pi R^2 dR/[1 + c \int_a^{R_q} g(R)4\pi R^2 dR] \quad (186)$$

At infinite dilution, $g(R) = \exp (be^{-\kappa R}/R)$. Linearizing the inner exponential and neglecting the second term in the denominator of the last equation we recover the Bjerrum result (Eq. (185)). However, at finite concentrations even if we retain terms to the same order in $\log \gamma_1$ and $g(R)$, Eqs. (183) and (186) will not in general give the same value of p. The use of a mass action formalism as a means both of calculating activity coefficients and of studying the pair distribution function via the degree of association p at finite concentrations is not done in a self-consistent manner in the Bjerrum type of treatment.

VII. MAYER'S FORMALISM FOR DEFECTS

We shall review briefly some aspects of Mayer's paper[59] on imperfect crystals. The treatment is in some ways complementary to the formalism used above and the programme he proposed, although so far not carried to completion by a numerical calculation, is of great interest. Mayer was principally concerned with the description and prediction of phase transitions, particularly melting, in crystals with short-range forces. However, the method is also of interest for crystals with relatively large degrees of intrinsic lattice disorder (see remarks in Section V-C).

The complete regularity of the arrangement of atoms in the space lattice of a perfect (point-defect-free) crystal allows a great simplification in the evaluation of the partition function since independent normal coordinates of vibration may be introduced.[10b] Born and his co-workers[9] have performed detailed calculations of the thermodynamic functions and elastic constants for monatomic solids of atoms interacting with the 6–12 potential and they found that the calculated equation of state indeed predicts that the lattice becomes unstable under certain conditions, presumably corresponding to the melting of the crystal. The Born procedure adequately describes the vibrational disorder but ignores the possible importance of configurational disorder, i.e. the formation of point defects such as vacant sites or interstitial atoms and their interactions. The theory of Lennard-Jones and Devonshire[48] stands at the other extreme. Here the formation of interstitial atoms leaving vacant sites is certainly considered, the configurational partition function being evaluated by the Bragg–Williams method,[33] and melting is associated with the sudden attainment of complete disorder with respect to lattice sites and interstitial positions. However, the calculation is carried through in a rather non-rigorous way with no attempt being made at precise calculation of defect formation and interaction energies and no account being taken of the vibrational disorder. Let us now consider Mayer's procedure against this background and the background of our remarks in Section V-C.

It is assumed that the temperature is sufficiently high for the "classical" form of partition function to be used:

$$Q(\mathbf{N},V,T) = (\mathbf{N}!\boldsymbol{\Lambda}^{\mathbf{N}})^{-1} \int d(\mathbf{N}) \exp(-U((\mathbf{N}))/kT) \quad (187)$$

where

$$\Lambda_s = (h^2/2\pi m_s kT)^{3/2} \quad (188)$$

m_s is the mass of an atom of type s and $U((\mathbf{N}))$ the potential energy of interaction of $\mathbf{N}$ atoms in the state $(\mathbf{N})$. ($\mathbf{N} = \mathbf{N}_0 + \mathbf{N}_a$ specifies the numbers of each of the $\sigma + \nu$ species of atoms present as in the first paragraph of Section II.) $(\mathbf{N})$ specifies both the site and the displacement from the centre of the site for each atom. A slight extension of the notation so far used proves convenient. The B sites of the crystal are labelled 1, 2, . . ., l, . . ., B and n_{sl} denotes the number of atoms of kind s on site number l. n_{0l} is defined to be 1 if site l is vacant and zero if it is occupied. Since we restrict configurations considered to those in which every site has only one atom or is vacant it follows that

$$\sum_{s=0}^{\sigma+\nu} n_{sl} = 1 \quad (189)$$

The set of occupation numbers, n_{sl}, which describe the state of every site in the crystal, is denoted by $\mathbf{n}$ and corresponds to a particular configuration $\{\mathbf{N}\}$. Corresponding to each $\mathbf{n}$ there are $\mathbf{N}!$ configurations differing only in the exchange of identical atoms between sites. Let $\mathbf{l}$ denote the coordinates of the atom at site l relative to the centre of the site and let $\{\mathbf{L}\}$ denote the set of all coordinates for every site of the crystal. If $n_{0l} = 1$ then fictitious coordinates are introduced. The partition function can now be written

$$Q(\mathbf{N},V,T) = (\boldsymbol{\Lambda}^{\mathbf{n}})^{-1} \sum_{\mathbf{n}}^{(\mathbf{N})} \int d\{\mathbf{L}\} \exp(-U_{\mathbf{n}}(\{\mathbf{L}\})/kT) \quad (190)$$

where for the vacant site we have defined

$$\Lambda_0 = v_0$$

where v_0 is the volume of a site. In fact Mayer prefers to work with the Grand Ensemble and this is readily seen to be

$$\begin{aligned} e^{pV/kT} &= \sum_{\mathbf{N}} \exp(\mathbf{N} \cdot \boldsymbol{\mu}/kT) Q(\mathbf{N},V,T) \\ &= \sum_{\mathbf{n}} \mathbf{z}^{\mathbf{n}} \int d\{\mathbf{L}\} \exp(-U_{\mathbf{n}}(\{\mathbf{L}\})/kT) \end{aligned} \quad (191)$$

the sum now being over every **n** consistent with every possible composition, instead of over a fixed composition as in (190). The activities, z, are defined by the equations

$$z_s = \exp(\mu_s/kT)/\Lambda_s, \qquad s \neq 0 \tag{192}$$

$$z_0 = \Lambda_0^{-1} \tag{193}$$

$$\mathbf{z}^{\mathbf{n}} = \prod_l \prod_s z_s^{\Lambda_{sl}} \tag{194}$$

Use of the Grand Ensemble has the disadvantage that all the calculated thermodynamic functions are dependent on **z**, V, and T. However, Mayer's programme can be adapted to the canonical ensemble (**N**, V, T).

Let **m** be the set of occupation numbers of the perfect crystal and define a quantity ν_{sl},

$$\nu_{sl} = n_{sl} - m_{sl} \tag{195}$$

which is zero unless the site l is occupied by a defect of species s. The ratio $\mathbf{z}^{\mathbf{n}}/\mathbf{z}^{\mathbf{m}}$ can then be written in the following form,

$$\mathbf{z}^{\mathbf{n}}/\mathbf{z}^{\mathbf{m}} = \mathbf{y}^{\boldsymbol{\nu}} = \prod_s \prod_l y_{s\lambda}^{\nu_{sl}} \tag{196}$$

where $y_{s\lambda}$ is the ratio of the activity of the defect of species s to the activity of the atom occupying the same site in the perfect crystal. The contribution of the point defects to the partition function can now be separated. Let $U_{\mathbf{m}}(\{\mathbf{L}\})$ be the potential energy of the occupation set **m** in the perfect crystal and define $U^*_{\boldsymbol{\nu}}(\{\mathbf{L}\})$ as

$$U^*_{\boldsymbol{\nu}}(\{\mathbf{L}\}) = U_{\mathbf{n}}(\{\mathbf{L}\}) - U_{\mathbf{m}}(\{\mathbf{L}\}) \tag{197}$$

The partition function is now

$$e^{pV/kT} = \mathbf{z}^{\mathbf{m}} \int d\{\mathbf{L}\} e^{-U_{\mathbf{m}}(\{\mathbf{L}\})/kT} \sum_{\boldsymbol{\nu}} \mathbf{y}^{\boldsymbol{\nu}} e^{-U^*_{\boldsymbol{\nu}}(\{\mathbf{L}\})/kT} \tag{198}$$

The essential feature of the Mayer method is that the configurational problem is solved first. In other words, we first evaluate the function $\Theta(\{\mathbf{L}\}, \mathbf{z}, T)$ defined by

$$e^{-\theta/kT} = e^{-U_{\mathbf{m}}(\{\mathbf{L}\})/kT} \sum_{\boldsymbol{\nu}} \mathbf{y}^{\boldsymbol{\nu}} e^{-U^*_{\boldsymbol{\nu}}(\{\mathbf{L}\})/kT} \tag{199}$$

For the perfect crystal Θ reduces to $U_{\mathbf{m}}(\{\mathbf{L}\})$ and the partition function is evaluated by expanding this potential energy in a

Taylor series in the displacements $\{\mathbf{L}\}$ of the atoms and taking full advantage of the crystal symmetry to perform a normal mode analysis. For the real crystal $\Theta(\{\mathbf{L}\})$ takes the place of the potential energy function. It contains contributions to the interactions between the occupants of each site in addition to those of $U_{\mathbf{m}}$, corresponding to the fact that the occupant of each site is no longer a "pure" atom of one species but has on average a certain amount of defect character, arising from the defects which can occupy that site and their interactions with other defects. However, Θ is still a periodic function so that in the remainder of the calculation the same methods can be used as for the perfect crystal and hence full advantage is taken of the crystal symmetry. The procedure may be contrasted with that used in principle in the other sections of this article, where one first averages over vibrational states and then tackles the configurational problem. The advantages of the latter procedure are:

(a) The configurational partition function and its expansion bear the greatest possible resemblance to those for an imperfect gas, and this is particularly convenient for Coulomb interactions. Further, the corresponding defect distribution functions are just those of interest in non-equilibrium measurements.

(b) The formalism is very simply related to the familiar quasi-chemical formulation for the calculation of defect concentrations. However, for a complete *a priori* calculation of thermodynamic properties one has to evaluate the partition function of the perfect crystal, Q_0, and the Q_c. For the latter one needs the defect formation and interaction free energies and hence a series of vibrational problems involving a crystal with one, two, . . . defects has to be solved. Such calculations are of course intrinsically interesting,[56] but if one is interested in phase transitions and thermodynamic properties when the degree of lattice imperfection is large then Mayer's procedure is the more economic of effort because full use is made of the crystal symmetry. As remarked at the beginning, the two schemes are complementary.

We should finally comment briefly on the calculation of Θ. For a crystal with short-range forces and hence short-range defect interactions a cluster expansion is convenient. Let $\{\mathbf{b}_\alpha\}_{\mathbf{B}}$ represent a particular subset, number α, of $\mathbf{b}$ sites out of the total of $\mathbf{B}$.

(There are $\binom{\mathbf{B}}{\mathbf{b}}$ such different subsets.) If $(\sum\{\mathbf{b}_\alpha\}_{\mathbf{B}})$ denotes the summation over all such subsets of $\mathbf{B}$ then we can write

$$\Theta(\{\mathbf{L}\}) = U_{\mathbf{m}}(\{\mathbf{L}\}) + (\sum\{\mathbf{b}_\alpha\}_{\mathbf{B}})\sigma(\{\mathbf{b}_\alpha\};\ \{\mathbf{L}\}) \tag{200}$$

According to Mayer it is reasonable to hope that σ functions for groups of up to four or five sites will prove sufficient to calculate Θ. Much of his paper is concerned with the derivation of a general formula which allows one to calculate the functions σ in terms of defect formation and interaction potential energies and details must be sought there. For example, for a crystal with a single species of impurity atom on only one kind of lattice site the general formula shows that σ for a single site, l, is given by

$$\exp(-\sigma((l);\ \{\mathbf{L}\})/kT) = y_l \exp(-U_l^*/kT) + 1 \equiv g_l \tag{201}$$

and for two sites k and l

$$\exp(-\sigma[(l,k);\ \{\mathbf{L}\}]/kT) = 1 + g_l g_k f_{lk}/(1 + g_l)(1 + g_k) \tag{202}$$

where

$$f_{lk} = \exp(-U_{lk}^*/kT) - 1 \tag{203}$$

U_l^* is the change in $U(\{\mathbf{L}\})$ on replacing the atom at site l in a perfect crystal by an impurity atom, and $(U_k + U_{kl})$ is the additional change on adding a further defect at site k. Note that g and f depend on the coordinates of the atoms relative to the site centres.

The establishment of a formula for the σ functions essentially involves solving the order–disorder problem in a suitable notation. Mayer's method is similar to that discussed by Domb and Hiley[20b] following earlier work of Rushbrooke and Scoins[76] and Fournet[20a]. We shall not discuss it in detail, but it may help to clarify the difference between the expansions of Section IV and that above by considering the evaluation of (cf. Eq. (78))

$$S = \sum_{\mathbf{n} \geqslant \mathbf{2}} \mathbf{c}_2^{\mathbf{n}} B_{\mathbf{n}} \tag{204}$$

for short-range interactions. At low concentrations the first two or three terms suffice but at higher concentrations where order–disorder theory is of interest, the most significant part of each

$B_{\mathbf{n}}$ must be kept. We may write the sum as

$$S = \sum_{m=1} S^{(m)} \tag{205}$$

where

$$S^{(m)} = \sum_{\mathbf{n} \geqslant \mathbf{2}} \mathbf{c}_2^{\mathbf{n}} B_{\mathbf{n}}^{(m)} \tag{206}$$

$$B_{\mathbf{n}} = \sum_{m=1} B_{\mathbf{n}}^{(m)} \tag{207}$$

$B_{\mathbf{n}}^{(m)}$ is the contribution to $B_{\mathbf{n}}$ of all the configurations in which $\mathbf{n}$ defects are assigned to m sites. The summation over m in Eq. (205) is essentially similar in character to that employed in Θ. Retention of only $m = 1$, 2 corresponds to the familiar quasi-chemical approximation of order–disorder theory.[33]

It should be clear that the Mayer method provides a convenient and economic framework within which to correct the major omissions inherent in the use of the crudest order–disorder results, e.g. the quasi-chemical and Bragg–Williams approximations, for crystals with short-range forces. However, detailed calculations by this method do not appear to have been attempted so far.

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DIMENSIONAL METHODS IN THE STATISTICAL MECHANICS OF IONIC SYSTEMS

M. BLANDER, *North American Aviation Science Center, Thousand Oaks, California*

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I. INTRODUCTION

The upsurge of interest in dense ionic systems has posed many problems in theoretical statistical mechanics. Many of these problems remain unsolved since the long-range nature of coulomb interactions has been a stumbling block in making rigorous calculations of the partition functions for these systems. Consequently, it is of interest to find methods of circumventing the difficulties in making statistical mechanical calculations. In this article I shall discuss the use of dimensional methods in solving some of the problems posed. In effect, rather than solving for

absolute values, dimensional methods lead to relative values of the partition functions. As we shall see, the relative values obtained have proven to be especially valuable in molten salt systems and appear to be useful in other ionic systems. In particular, dimensional methods have led to the only solution theory for dense ionic fluids which treats the coulomb interactions rigorously. The calculations are based upon an ingenious use of a well known property of ionic systems by Reiss, Mayer, and Katz[1] for the treatment of molten salts.

The discussion will be limited to systems at temperatures which are high enough so that we need only consider the classical partition function Q in calculating the Helmholtz free energy A, where, of course

$$A = -kT \ln Q \tag{1}$$

The partition function can be written as the product of K, the kinetic energy integral, and Z, the configurational integral,

$$Q = KZ \tag{2}$$

In all cases considered, differences in free energy for a given material in two different states or derivatives of the free energy are calculated and the contributions of the kinetic energy integrals to these quantities will exactly cancel. Since the results are not altered by its omission, for the sake of brevity, we shall not consider the kinetic energy integral.

If we consider a symmetric salt* of N cations and N anions then the configurational integral is

$$Z = \frac{1}{(N!)^2} \int \cdots \int_V \exp\left(-U/kT\right) (d\tau_c)^N (d\tau_a)^N \tag{3}$$

where U is the potential energy of a particular ionic configuration in which the ionic positions are specified by the volume elements $d\tau$, in configuration space,

$$(d\tau_c)^N = d\tau_{c1}, d\tau_{c2}, \ldots, d\tau_{ci}, \ldots d\tau_{cN}$$

and

$$(d\tau_a)^N = d\tau_{a1}, d\tau_{a2}, \ldots, d\tau_{ai}, \ldots d\tau_{aN}$$

* The treatment can be easily extended to other types of salts.

where c signifies cations and a anions. The total potential energy may be written as the sum of the pair potentials

$$U = \sum_c \sum_a u + \sum_{c<c'} \sum u' + \sum_{a<a'} \sum u'' \tag{4}$$

where u, u', and u'' are the cation–anion, cation–cation, and anion–anion pair potentials, respectively, and the summations are made such that the indices $c < c'$ and $a < a'$ insure that the sums are made in such a way that no pair potential is counted more than once. We shall show that by using a physically reasonable approximation,[1] we can cast the pair potentials u, u', and u'' into a form which is particularly convenient for the dimensional analysis of Z. This approximation is based on a concept similar to the Brönsted theory of specific ionic interaction in aqueous media.[2]

II. DIMENSIONAL ANALYSIS OF THE CONFIGURATIONAL INTEGRAL

A. Scaling of the Pair Potential

The cation–anion pair potential for a symmetrical salt may be written as the sum of the core repulsion and the coulomb interaction. For example, if the core repulsion is an inverse power potential, then*

$$u = \frac{A}{r^n} - \frac{e^2}{r} = \frac{e^2}{d}\left[\frac{1}{n}\left(\frac{d}{r}\right)^n - \frac{d}{r}\right] = \frac{1}{d} f\left(\frac{r}{d}\right) \tag{5}$$

where e is the electronic charge and d is the distance between ion centers at the minimum in their potential well. The coulomb repulsions of the ions of like sign have the same form as u

$$u' = u'' = \frac{e^2}{r} = \frac{e^2}{d}\left(\frac{d}{r}\right) = \frac{1}{d} f'\left(\frac{r}{d}\right) \tag{6}$$

* Experimental data on the compressibilities of solid salts appear to be consistent with the general form of the core repulsion part of the pair potential $(1/d)f(r/d)$ even for the exponential form.[3] Although for simplicity the equations are written for monovalent ions in a vacuum, they may easily be extended to other valence types and to ions contained in a dielectric.

At this point we introduce a physically reasonable approximation which makes the dimensional analysis possible. Coulomb repulsions between ions of like sign lead to a strong tendency toward local electroneutrality, and configurations in which two cations or two anions touch or are very close to each other have a relatively high potential. These configurations should make a very small contribution to the configurational integral* and consequently, in the most significant configurations, the contributions to the total potential of the core repulsions between ions of like sign are small and are assumed to be negligible. This results from the strong decrease of the core repulsions with r. Thus, the total potential U can be written in the form

$$U = \frac{1}{d} F\left(\frac{r}{d}\right) \tag{7}$$

since all of the individual pair potentials in the significant configurations have the same form.

Equation (7) can be applied to interactions of multivalent ions of valence z dissolved in a dielectric by multiplying the right-hand side by (z^2/D), where D is the dielectric constant of the medium. Equations (5) and (6) do not include ion–multipole and multipole–multipole interactions. A major part of these interactions may be represented by a pseudo dielectric constant which is relatively small and should not vary greatly from salt to salt in a given group.[5]

The choice of the size parameter d is somewhat ambiguous since even the relative values of d vary somewhat between solid, liquid, and gaseous salts because of the influence of interactions other than those represented by Eq. (7). For the case of a change of phase or for the description of phenomena where the environment of the ions changes drastically (as in the discussions of vapor pressure and surface tension), the influence of these other interactions is relatively large and other characteristic thermodynamic parameters (such as the melting temperature), which at least partly reflect these other interactions, should lead to more realistic relationships. Where there is no drastic change

* In molten salts, for example, this assumption is supported by X-ray and neutron-diffraction measurements. See Levy and Danford[4] for a discussion of this point.

of ionic environment (as in the case of ionic associations in the vapor phase), the actual measured interionic distances in the vapor should be good characteristic parameters. Such an approach is characteristic of corresponding-states treatments of nonelectrolytes.[6]

B. Scaling of the Configurational Integral

If we substitute from Eq. (7) into Eq. (3) then

$$Z = d^{6N} I[(dT), (V/d^3), (\mathscr{A}/d^2)] \tag{8}$$

where $\mathscr{A}$ is an interfacial area and I is the integral in Eq. (3) in which all distances and volumes are measured in units of d and d^3. Equation (8) is sufficient to derive relationships between thermodynamic properties of different salts in corresponding states.

It is probably instructive to derive Eq. (8) in a somewhat different way. Let us compare an arbitrary salt BY in which the characteristic size parameter is d with a "comparison salt" of the same valence type, AX, in which the size parameter is d_0 so that from Eq. (7)

$$U_0 = (1/d_0)\, F(r/d_0)$$

and

$$U = \frac{1}{d} F\left(\frac{r}{d}\right) = \left(\frac{d_0}{d}\right)\frac{1}{d_0} F\left(\frac{r}{d_0}\frac{d_0}{d}\right) = gU_0(gr) \tag{9}$$

where we have defined g by the relation

$$g \equiv d_0/d \tag{10}$$

The configurational integrals for these two salts are Z and Z_0. If the integral Z is over the volume V and Z_0 is over the volume V_0 so that $g^3V = V_0$, then for each configuration of the ions of BY in Z one can find a geometrically similar configuration for the ions of AX in Z_0 by multiplying all distances by the factor g. The potential energies of these two similar configurations are $U(r)$ and $U_0(gr)$, so that using Eq. (9) it is easy to show that

$$Z(T, V, \mathscr{A}) = \frac{1}{g^{6N}} Z_0\left(\frac{T}{g}, g^3V, g^2\mathscr{A}\right) \tag{11}$$

Equation (11) is an alternative way of expressing Eq. (8).

III. RELATIONSHIPS FOR ONE-COMPONENT SYSTEMS

In this section we shall discuss some relationships for pure compounds. Although the topics are limited to those which have been previously examined, many other properties can be treated by the calculational techniques discussed.

A. Corresponding-States Expressions for Vapor Pressures[1]

The vapor pressure, p, may be calculated from the equation:

$$p(T, V) = kT(\partial \ln Z/\partial V)_{T,N} \tag{12}$$

and

$$p(T, V) = \frac{k}{d^3}\frac{Td}{d}\left[\frac{\partial \ln Z(Td, V/d^3)}{\partial(V/d^3)}\right] = \frac{1}{d^4}p(Td, V/d^3) \tag{13}$$

and by defining

$$\pi = d^4p \tag{14a}$$

$$\tau = Td \tag{14b}$$

and

$$\theta = V/d^3 \tag{14c}$$

then Eqs. (13) and (14) lead to the reduced equation of state

$$\pi = \pi(\tau, \theta) \tag{15}$$

which is restricted to symmetrical salts for which the pair potentials can be written in the form of Eq. (7). Equation (15) may be termed a "molecular theory" reduced equation of state. If a dielectric constant appears in Eq. (7) then the expressions for π and τ are multiplied by D.

Alternative equations of state may be derived from Eq. (15). For example, one can obtain an equation of state in terms of variables expressed relative to their values at the melting point. At the melting point, the reduced variables π_m, τ_m, and θ_m are universal constants. This is illustrated in Table I where τ_m is given for several salts. Except for the lithium halides, which are not expected to follow this development since the small radius of the lithium ion leads to anion–anion contacts, τ_m is reasonably

constant in any given class of materials. For the alkali halides

$$T_m = (3 \times 10^{-5}/d) \text{ deg. K} \tag{16}$$

appears to hold.

TABLE I. Melting Points and Interatomic Distances for Symmetric Compounds[1]

Salt	Melting point T_m, °K	Interatomic distance in solid, cm $\times 10^8$	$dT_m/Z^2 = \tau_m$, cm. deg $\times 10^5$
MgO	3073	2.10	1.61
CaO	2873	2.40	1.73
SrO	2733	2.54	1.74
BaO	2198	2.75	1.51
NaF	1265	2.31	2.92
NaCl	1074	2.81	3.02
NaBr	1023	2.98	3.04
NaI	933	3.23	3.01
KF	1129	2.67	3.02
KCl	1045	3.14	3.28
KBr	1013	3.29	3.34
KI	958	3.53	3.39
RbF	1048	2.82	2.96
RbCl	988	3.29	3.26
RbBr	953	3.43	3.27
RbI	913	3.66	3.34
CsF	955	3.01	2.88
CsCl	918	3.47	3.18
CsBr	909	3.62	3.29
CsI	894	3.83	3.42
LiF	1121	2.01	2.25
LiCl	887	2.57	2.27
LiBr	823	2.75	2.27
LiI	718	3.02	2.21

If we define the new reduced variables

$$\begin{aligned} p/p_m &= \pi/\pi_m = \pi' \\ T/T_m &= \tau/\tau_m = \tau' \\ V/V_m &= \theta/\theta_m = \theta' \end{aligned} \tag{17}$$

then $$\pi' = \pi'(\tau', \theta') \tag{18}$$

is a new reduced "thermodynamic" equation of state. Equation (18) applies to salts for which the ion-pair potentials are more general than Eq. (7).

For a given class of salts the total potential (Eq. (7)) is a function of a single parameter, d (or g), and, consequently, the equation of state may be rewritten in terms of one thermodynamic parameter, e.g. the melting temperature, T_m. Substituting for d in Eqs. (14b) and (14c) from the expression

$$d = \tau_m / T_m \tag{19}$$

and remembering that τ_m is a universal constant, the new variables

$$\pi'' = \pi/\tau_m^4 = (p/T_m^4) \tag{20a}$$

$$\tau'' = \tau/\tau_m = T/T_m = \tau' \tag{20b}$$

$$\theta'' = \theta\tau_m^3 = T_m^3 V \tag{20c}$$

satisfy the universal relation

$$\pi'' = \pi''(\tau'', \theta'') \tag{21}$$

We shall now examine the consequences of Eqs. (18) and (21). For the case of two-phase vapor–liquid equilibria, there is only one degree of freedom and only one variable. Consequently, Eq. (18) leads to*

$$\pi' = \pi'(\tau') \tag{22}$$

Differentiating the logarithm of π' by $(1/\tau')$ one obtains

$$\frac{d \ln \pi'}{d(1/\tau')} = F(\tau') \tag{23}$$

$$\frac{d \ln \pi'}{d(1/\tau')} = \frac{d \ln p}{T_m d(1/T)} = -\frac{\Delta H_v}{RT_m} \tag{24}$$

from which one may deduce that at fixed values of τ' the quantity $\Delta H_v/T_m$ (and also the enthalpies of vaporization of monomers or dimers divided by T_m, $(\Delta H_{v1}/T_m)$ or $(\Delta H_{v2}/T_m)$) will be constant. Table II contains a listing of $\Delta H_{v1}/T_m$, which is the entropy of

* There are monomers, dimers and sometimes trimers in the vapors of alkali halides. It can be shown that Eq. (22) is valid not only for the total pressure but also for the partial pressures of each species.

TABLE II. Corresponding-States Vapor Pressures and Surface Tensions for Molten Alkali Halides

1[a]	2[a]	3[a]	4[a]	5[a]	6[a]	7[a]	8[a]	9[a]	10[a]	11[a]	12[a]	13[a]
NaF	1265	54.7	43.1	84.4	33.0	908	354	202	100	189	93	249
NaCl	1074	45.3	42.2	36.9	27.8	430	323	116	94	106	86	257
NaBr	1023	42.6	41.8	34.9	31.9	387	353	99	93	93	87	262
NaI	933	39.1	41.9	17.8	23.5	257	339	88	108	80	98	297
KF	1129	46.8	41.4	71.9	44.2	650	400	142	99	135	93	270
KCl	1045	43.7	41.9	42.4	35.5	467	392	99	87	91	80	306
KBr	1013	41.7	41.4	38.1	36.2	397	377	89	86	82	78	312
KI	958	39.9	41.8	27.8	33.1	300	357	79	90	71	81	348
RbF	1048	44.5	41.7	45.1	37.4	512	425	131	114	118	102	294
RbCl	988	42.3	42.5	26.6	27.9	308	323	99	103	91	94	352
RbBr	953	40.8	42.3	18.9	22.9	239	289	91	105	84	97	367
RbI	913	38.8	42.2	14.3	20.6	193	277	83	109	75	99	407
CsF	955	40.1	41.1	49.6	59.6	508	611	107	123	100	114	292
CsCl	918	40.7	44.3	21.1	29.7	242	340	90	116	85	109	376
CsBr	909	38.3	42.1	16.4	24.0	210	307	85	113	77	102	403
CsI	894	38.4	42.7	17.1	26.8	203	317	75	105	69	96	421
LiF	1121	55.3	49.3	7.1	4.5	143	91	251	178	241	171	204
LiCl	887	44.2	50.1	4.6	7.4	72	116	138	198	131	188	234
LiBr	823	42.1	51.2	2.4	5.3	44	97	—	—	—	—	—
LiI	718	38.3	51.6	0.2	0.8	10	37	—	—	—	—	—

[a] 1. Salt. 2. T_m(°K). 3. ΔH_{v1}. 4. $(\Delta H_{v1}/T_m)$. 5. Pressure at $1.30T_m$ (mm Hg). 6. $\pi''_{1.30}$ [mm (deg)$^{-4}$ $\times$ 10^{12}]. 7. Pressure at $1.55T_m$ (mm Hg). 8. $\pi''_{1.55}$ [mm (deg)$^{-4}$ $\times$ 10^{12}]. 9. σ at T_m (dyne cm^{-1}). 10. $\Sigma''_m(\times 10^9)$. 11. σ at $1.10T_m$ (dyne cm^{-1}). 12. $\Sigma''_{1.10}(\times 10^9)$. 13. Σ_m.

vaporization of the monomer from the liquid at the melting point. For all of these alkali halides excepting the lithium salts, these quantities, given in column 4 of Table II, are constant within the errors in the determination of the enthalpy of vaporization of the monomer, ΔH_{v1}.

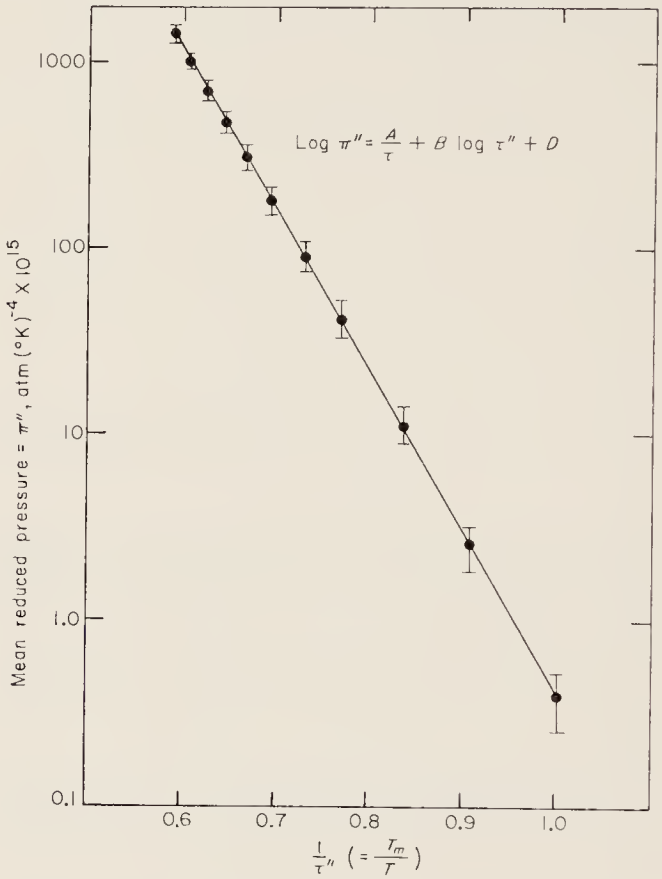

Fig. 1. Mean reduced vapor pressure curve for the halides of sodium, potassium, rubidium, and cesium. Average deviation from the mean is shown by the vertical lines.

Equation (21) for a two-phase equilibrium is

$$\pi'' = \pi''(\tau'') \tag{25}$$

In columns 6 and 8 of Table II are given values of π'' at $\tau'' = 1.30$ and 1.55* for all the alkali halides. The constancy of π'' at each

* Data were obtained from Kubaschewski and Evans.[7]

value of τ'' is good (except for the lithium salts). The mean deviation at $\tau'' = 1.30$ is 21% and at $\tau'' = 1.55$ it is 14%, which is good considering that the pressure is related exponentially to the free energy. In Fig. 1 are plotted mean values of $\log \pi''$ versus $1/\tau''$, where π'' is averaged for all except the lithium salts. A least-squares fit of the curve leads to the general equation for the alkali halides represented

$$\log_{10}\pi'' = -(9.20/\tau'') - 0.894 \log_{10} \tau'' - 6.21 \tag{26}$$

where π'' is in atmospheres (degrees)$^{-4}$. Equation (26) fits the points with an average deviation of 2%.

B. Surface Tension[1]

The surface tension, σ, may be treated by the method of corresponding states by use of the relation

$$\sigma = -kT(\partial \ln Z/\partial \mathscr{A})_{T,V,N} \tag{27}$$

From Eq. (8) we may derive the corresponding-states relation for the surface tension

$$\Sigma = d^3\sigma = \Sigma(\tau, \theta) \tag{28}$$

where Σ is the reduced surface tension. As in the case of pressure, we may introduce new reduced variables Σ' and Σ'' where

$$\Sigma' = \Sigma/\Sigma_m \tag{29}$$

and

$$\Sigma'' = (\sigma/T_m^3) \tag{30}$$

which are universal functions of τ' $(= \tau'' = T/T_m)$ and θ' (or θ''). Values of Σ_m are tabulated in column 13 of Table II and of Σ_m'' and $\Sigma_{1.10}''$ in columns 10 and 12. Σ_m is evaluated at the melting point and Σ_m'' and $\Sigma_{1.10}''$ are the values of Σ'' at the melting temperature, T_m, and at $1.10T_m$. The constancy of Σ_m is not good, which is a reflection of the high sensitivity of this quantity to uncertainties in d and to interactions other than are consistent with Eq. (7). On the other hand, Σ_m'' and $\Sigma_{1.10}''$ are quite constant, indicating the utility of the "thermodynamic" reduced surface tension in Eq. (30).

C. Association in Alkali Halide Vapors

Many investigations of salt vapors have demonstrated that alkali halide vapor molecules associate.[8] Theoretical calculations concerning the relatively simple dimers have been very difficult and have required a large amount of input data. Calculations concerning the trimers are even more difficult and have never been attempted. The techniques of dimensional analysis can be of value in reducing the amount of input data necessary and also in making possible the calculation of relative quantities where the systems could not be treated otherwise.[9]

We shall examine the simplest association in the vapor phase, dimerization. Any conclusions drawn may be extended to higher polymerizations. For the "comparison" salt AX, which has a characteristic size parameter d_0, the association constant for the equilibrium

$$2\,\mathrm{AX} \rightleftarrows \mathrm{A_2X_2} \tag{31}$$

is K_{20} and the standard Helmholtz free energy of dimerization, ΔA_{20}, is calculated from the equation

$$\Delta A_{20} = -RT \ln K_{20} \tag{32}$$

where K_{20} is in reciprocal concentration units (liters/mole). The salt BY, with a characteristic size parameter d, which is to be compared with AX has a dimerization constant K_2, where K_2 may be expressed as

$$K_2 = VZ_2/Z_1^2 \tag{33}$$

where Z_2 is the configurational integral for two molecules of BY in a volume V and Z_1 is for one molecule of BY

$$Z_1 = \int\int \exp(-u/kT)d\tau_c d\tau_a \tag{34}$$

$$Z_2 = \int \cdots \int \exp(-U_2/kT)d\tau_c d\tau_a d\tau_{c'} d\tau_{a'} \tag{35}$$

where u is the cation–anion pair potential and U_2 is the sum of the pair potentials

$$U_2 = u_{ac} + u_{a'c} + u_{ac'} + u_{a'c'} + u'_{cc'} + u''_{aa'} \tag{36}$$

between the two cations c and c' and the two anions a and a'.

By a dimensional analysis of V, Z_1, and Z_2 as is given in detail in Section II which utilizes the expressions

$$u = gu_0(gr) \tag{37}$$

and

$$U_2 \cong gU_{20}(gr) \tag{38}$$

we arrive at an expression for K_2 in terms of the function K_{20}

$$\ln K_2(T) + 3 \ln g = \ln K_{20}(T/g) \tag{39}$$

which is the law of corresponding states for dimerization. For the formation of an n'mer from the monomer, we obtain the relation for the association constant K_n

$$\ln K_n(T) + 3(n - 1) \ln g = \ln K_{n0}(T/g) \tag{40}$$

In column 5 of Table III are given values of $\log K_2(1365g) + 3 \log g$ for seven salts for which reliable data are available.[10] Sodium iodide has been chosen as the "comparison" salt. The temperature $1365g$ is chosen so that T/g is a constant and consequently $\log K_2 + 3 \log g$ should be constant. The constancy of the quantities in column 5 is well within the experimental uncertainties of the data and supports the validity of Eq. (39) and also supports the potential usefulness of Eqs. (39) and (40) in making predictions for alkali halide vapors.

Other useful expressions may be obtained from Eqs. (39) and (40) by expanding the right-hand sides in a series in $(g - 1)$. For example, if the right-hand side of (39) is expanded, we obtain:

$$\ln K_{20}(T/g) = \ln K_{20}(T) + \left(\frac{\partial \ln K_{20}(T/g)}{\partial g}\right)_{g=1} (g - 1) + \frac{1}{2}\left(\frac{\partial^2 \ln K_{20}(T/g)}{\partial g^2}\right)_{g=1} (g - 1)^2 + \ldots \tag{41}$$

The derivatives are evaluated as follows

$$\left(\frac{\partial \ln K_{20}(T/g)}{\partial g}\right)_{g=1} = \left(\frac{\partial \ln K_{20}}{\partial (g/T)}\right)_{g=1} \left(\frac{\partial (g/T)}{\partial g}\right) = \frac{1}{T} \frac{\partial \ln K_{20}(T)}{\partial (1/T)} = \frac{-\Delta E_{20}}{RT} \tag{42}$$

TABLE III. Comparison of the Measured with the Calculated Thermodynamic Properties of Some Associating Alkali Halides

Salt	d	g	log $K_2(1365g)$	log $K_2(1365g)$ $+3 \log g$	log K_2(1300°K)		$-\Delta E_2$, kcal/mole		$-\Delta S_{2p}$, cal/deg mole	
					Meas.	Calc.	Meas.	Calc.	Meas.	Calc.
NaCl	2.3606	1.149	3.00	3.18	4.378	4.132	48.0	46.2	28.3	27.9
NaBr	2.5020	1.084	2.83	2.93	3.710	3.775	42.9	43.6	28.8	27.6
NaI	2.7115	1.000	2.99	(2.99)	3.312	(3.312)	40.2	(40.2)	27.1	(27.1)
KCl	2.6666	1.017	3.06	3.08	3.500	3.406	41.2	40.9	27.1	27.2
KI	3.0478	0.890	3.25	3.10	2.846	2.722	34.7	35.8	25.0	26.4
RbCl	2.7867	0.973	2.99	2.95	3.130	3.166	39.4	39.1	27.3	26.9
CsCl	2.9062	0.933	2.91	2.82	2.790	2.950	34.7	37.5	25.3	26.7

$$\left(\frac{\partial^2 \ln K_{20}(T/g)}{\partial g^2}\right)_{g=1} = \left(\frac{\partial^2 \ln K_{20}}{\partial (g/T)^2}\right)_{g=1} \left(\frac{\partial (g/T)}{\partial g}\right)^2 = \frac{\Delta C_V}{R} \quad (43)$$

where ΔE_{20} and ΔC_V are the standard energy and heat capacity changes upon dimerization of the "comparison" salt. If we combine Eqs. (39) and (41)–(43) we obtain

$$\ln K_2(T) = -3 \ln g + \ln K_{20}(T) - \frac{\Delta E_{20}}{RT}(g-1) + \frac{\Delta C_V}{2R}(g-1)^2 + \ldots \quad (44)$$

$$\ln K_2(T) = -3 \ln g + \frac{\Delta S_{20}}{R} - \frac{g \Delta E_{20}}{RT} + \frac{\Delta C_V}{R}(g-1)^2 + \ldots \quad (45)$$

where ΔS_{20} is the standard entropy of dimerization of the comparison salt. If the association constants are in pressure units, then Eqs. (44) and (45) become

$$\ln K_{2p}(T) = -3 \ln g + \ln K_{2p0}(T) - \frac{\Delta E_{20}}{RT}(g-1) + \ldots \quad (46)$$

$$\ln K_{2p}(T) = -3 \ln g + \frac{\Delta S_{20}}{R} + (1 + \ln R^* T) - \frac{g \Delta E_{20}}{RT} + \ldots \quad (47)$$

where the sum of the first three terms on the right of Eq. (47) is $(\Delta S_{2p}/R)$, where ΔS_{2p} is the standard entropy of association. If the standard states are chosen as the ideal gas monomer and dimer at one atmosphere, R is in calories/degree-mole, R^* is the gas constant in liter-atmospheres/degree-mole, and K_{2p} is in reciprocal atmospheres. From Eqs. (44) and (46) we may deduce the association constants for one salt at a given temperature from those of a known "comparison" salt at the same temperature. Equations (45) and (47) lead to the relations between entropies and between energies of association

$$\Delta E_2 = g \Delta E_{20} \quad (48)$$

$$\Delta S_{2p} = \Delta S_{2p0} - 3 \ln g \quad (49)$$

Columns 6 and 7 of Table III give a test of Eq. (44) using data available on seven alkali halides.[10] Using NaI as the comparison salt, the values of log $K_2(1300)$ given in column 7 were calculated

from Eq. (44) and are to be compared with the measured values given in column 6. A value of $\Delta E_{20} = 40.2$ kcal/mole was used in the calculations. The agreement is excellent and within the errors in the measurements. Columns 8 and 9 of Table III,[10] and Table IV[8] give a test of Eq. (48) using NaI as the comparison

TABLE IV. Comparison of Measured and Calculated Values of the Energy of Association (in kilocalories/mole). The calculated values are given in brackets and are equal to $g\Delta E_{20}$, where ΔE_{20} is the energy of association of NaI, 39.5 kcal/mole. Values of d were obtained from Ref. 9 for all salts except LiF and KF. For LiF they were obtained from Wharton, L. *et al.*, *J. Chem. Phys.* **38**, 1203 (1963) and for KF from Green, G. W., and Lew, H., *Can. J. Phys.* **38**, 482 (1960)

	Li	Na	K	Rb	Cs
F	60.0 [68.5]	55.5 [55.6]	49.0 [49.3]	44.0 [47.3]	38.5 [45.7]
Cl	50.0 [53.0]	46.0 [45.4]	41.0 [40.2]	38.0 [38.4]	35.0 [36.9]
Br	45.0 [49.3]	43.5 [42.8]	– [38.0]	– [36.4]	– [34.9]
I	41.5 [44.8]	39.5 [39.5]	35.5 [35.2]	– [33.7]	– [32.3]

salt. Except for LiF and CsF, the agreement is within the uncertainties in the experimental data. Columns 10 and 11 of Table III give a test of Eq. (49). The dependence of ΔS_{2p} on g is significant and is as predicted by Eq. (49).

The very simple equations (44)–(49) should be useful in making predictions where data are not available and should be valuable in avoiding complicated and cumbersome calculations.

IV. CONFORMAL IONIC SOLUTION THEORY

A. Introduction

Conformal ionic solution theory was the first theory applied to molten salts which rigorously took coulomb interactions into

account. The method of calculation was first used by Reiss, Katz, and Kleppa[11] and consists of a perturbation theory similar to conformal solution theory for non-electrolytes.[12] Although the original derivation was restricted to salts consisting of hard charged spheres, it has been shown that the theory applies to systems in which the pair potentials have a more general form.[13] One begins with a "comparison" salt with the characteristic size parameter d_0. By varying the ion sizes of the "comparison" salt one may produce other pure salts or a mixture. A calculation of the free energy changes produced by these variations in ionic size can be made and used to calculate solution properties.

B. Calculations for Binary Mixtures

One begins with the configurational integral for the "comparison" salt*

$$\begin{aligned} Z_0 &= (1/N!)^2 \int \cdots \int \exp(-U_0/kT)(d\tau_c)^N(d\tau_a)^N \\ &= (1/N!)^2 Z_0' \end{aligned} \tag{50}$$

where the total potential energy U_0 of a given configuration of the ions is given by

$$U_0 = \sum_c \sum_a u_0 + \sum_{c<c'} \sum u_0' + \sum_{a<a'} \sum u_0'' \tag{51}$$

In order to calculate the free energy of mixing for a mixture consisting of the two cations A^+ and B^+ and the anion X^-, three separate perturbation calculations are carried out. If AX is salt 1 and BX salt 2, then there are two size parameters (or characteristic sums of cation–anion radii) d_1 and d_2. Dimensionless perturbation parameters are defined by

$$d_0/d_i = g_i \tag{52}$$

The procedure begins with three separate samples of the "comparison" salt, which in this case has X^- as the anion. The sizes of the cations are changed so that in one sample d_0 changes to d_1, in a second sample d_0 changes to d_2, and in a third sample

* A prime on Z denotes the configurational integral without the factorial coefficients. This notation is introduced to simplify expressions which appear later.

a fraction X_1 of the cations change in size so that d_0 changes to d_1 and a fraction X_2 $(= 1 - X_1)$ change so that d_0 changes to d_2. In the first two samples, the pure components 1 and 2 result and in the third a mixture results. The changes in the potential energies of a given configuration, in the configurational integrals, and in the Helmholtz free energies for these cases are written as

$$\begin{array}{lll} U_0 \rightarrow U_1 & U_0 \rightarrow U_2 & U_0 \rightarrow U_m \\ Z_0 \rightarrow Z_1 & Z_0 \rightarrow Z_2 & Z_0 \rightarrow Z_m \\ A_0 \rightarrow A_1 & A_0 \rightarrow A_2 & A_0 \rightarrow A_m \end{array} \tag{53}$$

where

$$\begin{aligned} A_i &= -kT \ln Z_i \\ A_m &= -kT \ln Z_m \end{aligned} \tag{54}$$

$$\begin{aligned} Z_i &= (1/N!)^2 \int \cdots \int \exp(-U_i/kT)(d\tau_c)^N (d\tau_a)^N \\ &\equiv (1/N!)^2 Z_i' \end{aligned}$$

$$\begin{aligned} Z_m &= \frac{1}{N!N_A!N_B!} \int \cdots \int \exp(-U_m/kT)(d\tau_c)^N (d\tau_a)^N \\ &\equiv \frac{1}{N!N_A!N_B!} Z_m' \end{aligned} \tag{55}$$

and where U_i and U_m are the total potential energies of a given configuration of the ions of salt i and of the mixture respectively. Since the only quantities which depend on the size parameters (or the perturbation parameters g_i) in the integrals in Eq. (55) are the total potential energies, we may evaluate the dependence of the Helmholtz free energy on g_i by analyzing the functional dependence of the total potential energy on the perturbation parameters. Knowing this functional dependence, we may evaluate the coefficients in a power series expansion of A_i and A_m about A_0. From A_i and A_m we may evaluate the total Helmholtz free energy of mixing of the binary mixture from the equation

$$\Delta A_m = A_m - X_1 A_1 - X_2 A_2 \tag{56}$$

The total potential energy of a given configuration may be written as the sum of the pair potentials. Each pair potential is

expressed as the sum of two types of terms for the class of *conformal ionic mixtures* we shall treat. One type of term is dependent only on r, the distance between ion centers, and is independent of which particular ionic species are involved. These terms include all coulomb interactions, and for the case in which the cations have equal (or negligibly small) polarizabilities, it also includes all ion–multipole and multipole–multipole interactions. Thus, for any given configuration of the ions of the "comparison" salt, a change of the size parameter d_0 to d_i for any given pair of ions (and of the perturbation parameter from unity to some value g_i) has no effect on this first type of interaction. This results from the fact that a given configuration is defined by fixing the centers of the ions in particular volume elements, $d\tau$, so that the variation in ion sizes does not change r.

The second type of interaction is dependent on the ion sizes and for the cation–anion pairs on the perturbation parameter, g_i. The core repulsive potential for a cation–anion pair has the form

$$g_i f(g_i r).$$

Because of coulomb repulsions, the core repulsive potential between ions of like sign may be assumed to be negligibly small in the most significant configurations (see Section II-A). Consequently, in these configurations, the interaction potential between ions of like sign is a function only of the distance between the ions and is independent of the type of ions. The cation–anion pair potentials may be written as

$$u_i = g_i f(g_i r) + h_i(r),\ h_i(r) = h_2(r) = h_0(r) = h(r) \qquad (57)$$

For the pure salt i we may write the total potential as

$$U_i = \sum_{c}^{N}\sum_{a}^{N} g_i f(g_i r) + \sum_{c}^{N}\sum_{a}^{N} h(r) + \sum_{c<c'}\sum u'(r) + \sum_{a<a'}\sum u''(r) \qquad (58)$$

and for the mixture as

$$U_m = \sum_{c}^{X_A N}\sum_{a}^{N} g_1 f(g_1 r) + \sum_{c}^{X_B N}\sum_{a}^{N} g_2 f(g_2 r) + \sum_{c}^{N}\sum_{a}^{N} h(r) + \sum_{c<c'}\sum u'(r) + \sum_{a<a'}\sum u''(r) \qquad (59)$$

If we now expand the free energies A_i and A_m in a MacLaurin series in $(g_i - 1)$ about A_0

$$-\frac{A_i}{kT} = \ln Z_i = \ln Z_0 + \left(\frac{\partial \ln Z_i}{\partial g_i}\right)_{g_i=1}(g_i - 1) + \frac{1}{2}\left(\frac{\partial^2 \ln Z_i}{\partial g_i^2}\right)_{g_i=1}(g_i - 1)^2 + \ldots \quad (60)$$

$$= \frac{A_m}{kT} = \ln Z_m = -X_A N \ln X_A - X_B N \ln X_B + \ln Z_0 + \left(\frac{\partial \ln Z_m}{\partial g_1}\right)_{g=1}(g_1 - 1) + \left(\frac{\partial \ln Z_m}{\partial g_2}\right)_{g=1}(g_2 - 1) + \frac{1}{2}\left(\frac{\partial^2 \ln Z_m}{\partial g_1^2}\right)_{g=1}(g_1 - 1)^2 + \left(\frac{\partial^2 \ln Z_m}{\partial g_1 \partial g_2}\right)_{g=1}(g_1 - 1)(g_2 - 1) + \frac{1}{2}\left(\frac{\partial^2 \ln Z_m}{\partial g_2^2}\right)_{g=1}(g_2 - 1)^2 + \ldots \quad (61)$$

We may evaluate the derivatives which appear in Eqs. (60) and (61). The designation $g = 1$ on the derivatives in Eq. (61) means the limit when the values of all the g_i are unity. The first coefficient in Eq. (60) is evaluated as follows

$$\left(\frac{\partial \ln Z_i}{\partial g_i}\right)_{g_i=1} = \frac{1}{Z_0'}\left(\frac{\partial Z_i'}{\partial g_i}\right)_{g=1} \quad (62)$$

$$\left(\frac{\partial Z_i'}{\partial g_i}\right)_{g_i=1} = -\frac{1}{kT}\int \ldots \int \left(\frac{\partial U_i}{\partial g_i}\right)_{g_i=1} \exp\left(-U_0/kT\right)(d\tau_c)^N (d\tau_a)^N$$

$$= -\frac{1}{kT}\int \ldots \int \sum_c^N \sum_a^N \varphi \exp\left(-U_0/kT\right)(d\tau_c)^N (d\tau_a)^N \quad (63)$$

where

$$\varphi = f + r\frac{\partial f}{\partial r} \quad (64)$$

Each of the N^2 terms in the double sum on the right of Eq. (63) represents a particular pair, and when each of them is integrated over all possible configurations it leads to the same result. Consequently

$$\left(\frac{\partial Z_i'}{\partial g_i}\right)_{g_i=1} = -\frac{N^2}{kT}\int \ldots \int \varphi \exp\left(-U_0/kT\right)(d\tau_a)^N (d\tau_c)^N = \mathrm{A} \quad (65)$$

The second derivative in Eq. (60) is given by

$$\left(\frac{\partial^2 \ln Z_i}{\partial g_i^2}\right)_{g_i=1} = \frac{1}{Z_0'}\left(\frac{\partial^2 Z_i'}{\partial g_i^2}\right)_{g_i=1} - \frac{1}{(Z_0')^2}\left(\frac{\partial Z_i'}{\partial g_i}\right)^2_{g_i=1} \tag{66}$$

and

$$\begin{aligned}\left(\frac{\partial^2 Z_i'}{\partial g_i^2}\right)_{g_i=1} &= -\frac{1}{kT}\int\cdots\int\left(\frac{\partial^2 U_i}{\partial g_i^2}\right)_{g_i=1}\exp(-U_0/kT)(d\tau_a)^N(d\tau_c)^N \\ &+ \left(\frac{1}{kT}\right)^2\int\cdots\int\left(\frac{\partial U_i}{\partial g_i}\right)_{g_i=1}\left(\frac{\partial U_i}{\partial g_i}\right)_{g_i=1}\exp(-U_0/kT)(d\tau_a)^N(d\tau_c)^N \\ &= -\frac{1}{kT}\int\cdots\int\sum_c^N\sum_a^N\Psi\exp(-U_0/kT)(d\tau_a)^N(d\tau_c)^N \\ &+ \left(\frac{1}{kT}\right)^2\int\cdots\int\sum_c^N\sum_a^N\sum_c^N\sum_a^N\varphi\varphi'\exp(-U_0/kT)(d\tau_a)^N(d\tau_c)^N \end{aligned} \tag{67}$$

where

$$\Psi = 2r\frac{\partial f}{\partial r} + r^2\frac{\partial^2 f}{\partial r^2}.$$

There are N^2 terms in the summation in the first term on the right-hand side of Eq. (67) all of which when integrated over all possible configurations are equal. In the second integral, there are four types of terms, all members of any type when integrated being equal. There are N^2 terms in which φ and φ' refer to the same cation–anion pair, which we designate as $\varphi_{ca}\varphi_{ca}$; there are $N^2(N-1)$ terms in which φ and φ' refer to two different cations and the same anion, which we designate as $\varphi_{ca}\varphi_{c'a}$; there are $N^2(N-1)$ terms in which φ and φ' refer to the same cation and two different anions, designated as $\varphi_{ca}\varphi_{ca'}$; and there are $N^2(N-1)^2$ terms in which φ and φ' refer to two different cations and two different anions, designated as $\varphi_{ca}\varphi_{c'a'}$. Consequently

$$\begin{aligned}\left(\frac{\partial^2 Z_i'}{\partial g_i^2}\right)_{g_i=1} &= N^2(\mathbf{B}+\mathbf{C}) + N^2(N-1)\mathbf{D} \\ &\quad + N^2(N-1)\mathbf{E} + N^2(N-1)^2\mathbf{F} \\ &= N^2(\mathbf{B}+\mathbf{C}-\mathbf{D}-\mathbf{E}+\mathbf{F}) + N^3(\mathbf{D}-\mathbf{F}) \\ &\quad + N^3(\mathbf{E}-\mathbf{F}) + N^4(\mathbf{F}) \end{aligned} \tag{68}$$

where

$$\mathbf{B} = -\left(\frac{1}{kT}\right)\int\cdots\int\Psi\exp(-U_0/kT)(d\tau_a)^N(d\tau_c)^N \tag{69}$$

$$\mathbf{C} = \left(\frac{1}{kT}\right)^2 \int \cdots \int \varphi_{ca}\varphi_{ca} \exp\left(-U_0/kT\right)(d\tau_a)^N(d\tau_c)^N \tag{70}$$

$$\mathbf{D} = \left(\frac{1}{kT}\right)^2 \int \cdots \int \varphi_{ca}\varphi_{c'a} \exp\left(-U_0/kT\right)(d\tau_a)^N(d\tau_c)^N \tag{71}$$

$$\mathbf{E} = \left(\frac{1}{kT}\right)^2 \int \cdots \int \varphi_{ca}\varphi_{ca'} \exp\left(-U_0/kT\right)(d\tau_a)^N(d\tau_c)^N \tag{72}$$

and $$\mathbf{F} = \left(\frac{1}{kT}\right)^2 \int \cdots \int \varphi_{ca}\varphi_{c'a'} \exp\left(-U_0/kT\right)(d\tau_a)^N(d\tau_c)^N \tag{73}$$

To simplify the notation we define

$$\mathbf{J} = N^2(\mathbf{B} + \mathbf{C} - \mathbf{D} - \mathbf{E} + \mathbf{F}) \tag{74}$$

$$\mathbf{K} = N^2(\mathbf{D} - \mathbf{F}) \tag{75}$$

$$\mathbf{L} = N^2(\mathbf{E} - \mathbf{F}) \tag{76}$$

$$\mathbf{M} = N^2\mathbf{F} \tag{77}$$

so that

$$\left(\frac{\partial^2 Z_i'}{\partial g_i^2}\right)_{g_i=1} = \mathbf{J} + N\mathbf{K} + N\mathbf{L} + N^2\mathbf{M} \tag{78}$$

Combining Eqs. (60), (62), (65), (66), and (78) we obtain for the Helmholtz free energy of the pure salt

$$-\frac{A_i}{kT} = \ln Z_0 + \frac{\mathbf{A}}{Z_0}(g_i - 1) + \frac{1}{2}\left[\frac{1}{Z_0'}(\mathbf{J} + N\mathbf{K} + N\mathbf{L} + N^2\mathbf{M}) - \left(\frac{\mathbf{A}}{Z_0'}\right)^2\right](g_i - 1)^2 + \cdots \tag{79}$$

The derivatives in Eq. (61) for the mixture may be evaluated as follows

$$\left(\frac{\partial \ln Z_m}{\partial g_1}\right)_{g=1} = \frac{1}{Z_0'}\left(\frac{\partial Z_m'}{\partial g_1}\right)_{g=1}$$

$$= -\frac{1}{Z_0' kT}\int \cdots \int \left(\frac{\partial U_m}{\partial g_1}\right)_{g=1} \exp\left(-U_0/kT\right)(d\tau_a)^N(d\tau_c)^N$$

$$= -\frac{1}{Z_0' kT}\int \cdots \int \sum_{c}^{X_A N} \sum_{a}^{N} \varphi \exp\left(-U_0/kT\right)(d\tau_a)^N(d\tau_c)^N$$

$$= X_{\mathrm{A}} \frac{\mathbf{A}}{Z'_0} \tag{80}$$

and

$$\left(\frac{\partial \ln Z_m}{\partial g_2}\right)_{g=1} = X_{\mathrm{B}} \frac{\mathbf{A}}{Z'_0} \tag{81}$$

$$\left(\frac{\partial^2 \ln Z_m}{\partial g_1^2}\right)_{g=1} = \frac{1}{Z'_0}\left(\frac{\partial^2 Z'_m}{\partial g_1^2}\right) - \frac{1}{Z'^2_0}\left(\frac{\partial Z'_m}{\partial g_1}\right)^2 \tag{82}$$

$$\left(\frac{\partial^2 \ln Z_m}{\partial g_1 \partial g_2}\right)_{g=1} = \frac{1}{Z'_0}\left(\frac{\partial^2 Z'_m}{\partial g_1 \partial g_2}\right)_{g=1} - \frac{1}{Z'^2_0}\left(\frac{\partial Z'_m}{\partial g_1}\right)_{g=1}\left(\frac{\partial Z'_m}{\partial g_2}\right)_{g=1} \tag{83}$$

where

$$\left(\frac{\partial^2 Z'_m}{\partial g_1^2}\right) = -\frac{1}{kT}\int \cdots \int \left(\frac{\partial^2 U_m}{\partial g_1^2}\right)_{g=1} \exp\left(-U_0/kT\right)(d\tau_a)^N (d\tau_c)^N + \left(\frac{1}{kT}\right)^2 \int \cdots \int \left(\frac{\partial U_m}{\partial g_1}\right)_{g=1}\left(\frac{\partial U_m}{\partial g_1}\right)_{g=1} \times \exp\left(-U_0/kT\right)(d\tau_a)^N (d\tau_c)^N \tag{84}$$

$$= X_{\mathrm{A}}\mathbf{J} + X_{\mathrm{A}}^2 N\mathbf{K} + X_{\mathrm{A}} N\mathbf{L} + X_{\mathrm{A}}^2 N^2\mathbf{M}$$

and

$$\left(\frac{\partial^2 Z'_m}{\partial g_2^2}\right)_{g=1} = X_{\mathrm{B}}\mathbf{J} + X_{\mathrm{B}}^2 N\mathbf{K} + X_{\mathrm{B}} N\mathbf{L} + X_{\mathrm{A}}^2 N^2\mathbf{M} \tag{85}$$

and

$$\left(\frac{\partial^2 Z'_m}{\partial g_1 \partial g_2}\right)_{g=1} = X_{\mathrm{A}} X_{\mathrm{B}} N\mathbf{K} + X_{\mathrm{A}} X_{\mathrm{B}} N^2\mathbf{M} \tag{86}$$

Terms in **J** and **L** do not appear in Eq. (86) since the terms designated $\varphi_{ca}\varphi_{ca}$ and $\varphi_{ca}\varphi_{ca'}$ both refer to only one cation. Since any given cation cannot be dependent on both g_1 and g_2 then $\varphi_{ca}\varphi_{ca}$ and $\varphi_{ca}\varphi_{ca'}$ terms cannot appear in the product $(\partial U_m/\partial g_1)_{g=1} \times (\partial U_m/\partial g_2)_{g=1}$ and consequently the terms **B**, **C**, and **D** of Eqs. (69)–(71) do not appear in the evaluation of $(\partial^2 Z'_m/\partial g_1 \partial g_2)_{g=1}$.

Combining Eqs. (56), (61), and (79)–(86) one obtains the equation for the total excess free energy of mixing, ΔA_m^E

$$\frac{-\Delta A_m^E}{kT} \equiv X_{\mathrm{A}} N \ln X_{\mathrm{A}} + X_{\mathrm{B}} N \ln X_{\mathrm{B}} - \frac{\Delta A_m}{kT}$$

$$= \tfrac{1}{2} X_A X_B \left[\frac{1}{Z_0'} (N\mathbf{K} + N^2\mathbf{M}) - (\mathbf{A}/Z_0')^2 \right] (g_1 - g_2)^2 + \ldots$$

$$= X_A X_B \Gamma(T, V)(g_1 - g_2)^2 \qquad (87)$$

Thus, in the free energy of mixing of a binary system, the first-order terms cancel each other and do not appear. All of the integrals contained in the terms Z_0', $\mathbf{A}$, $\mathbf{K}$, $\mathbf{M}$, and Γ in Eq. (87) are dependent solely on the properties of the "comparison" salt and are constant for binary conformal ionic mixtures having X^- as the anion.

C. Discussion of Binary Mixtures

Equation (87) and analogous equations for ΔG_m^E, ΔH_m, and for surface tensions apply to molten salt mixtures in which the interaction potential can be classed as conformal. These relations may also be used to test whether the ionic interaction potential in aqueous solutions may be considered as conformal. Thus, as will be shown in one simple example, the limits of usefulness of some interionic interaction potentials may be tested in ranges of concentration of salts in water too high to obtain absolute values for the partition functions. A similar test may be made for associations in salt vapors such as

$$A_2X_2 + B_2X_2 \rightleftarrows 2\,ABX_2$$

By simple thermodynamic arguments Brown[14] has shown that, consistent with the accuracy of this second-order approximation, one may obtain from the form of Eq. (87) the form of the excess Gibbs free energy of mixing (ΔG_m^E), the enthalpy of mixing of a molten salt (ΔH_m), and the deviation of the surface tension from linearity:

$$\Delta G_m^E = X_1 X_2 \theta(T, P)(g_1 - g_2)^2 + \ldots \qquad (88)$$

$$\Delta H_m = X_1 X_2 \Omega(T, P)(g_1 - g_2)^2 + \ldots \qquad (89)$$

$$\sigma_m - X_1\sigma_1 - X_2\sigma_2 = X_1 X_2 \varepsilon(g_1 - g_2)^2 + \ldots \qquad (90)$$

where σ_m is designated as the surface tension of the mixture. The most conclusive test of the theory has been made by comparing the measurements of the enthalpies of mixing of molten alkali nitrates with Eq. (89).[15] Figure 2 contains a plot of the enthalpy of mixing of nine different 50–50 mole % solutions of alkali

nitrates versus the parameter $(d_2 - d_1)^2/(d_1 d_2)^2$ (which is proportional to $(g_1 - g_2)^2$). The agreement with theory is excellent. A similar test of Eq. (90) has been made by Bertozzi and Sternheim[16] on mixtures of alkali nitrates. The agreement with theory is again excellent.

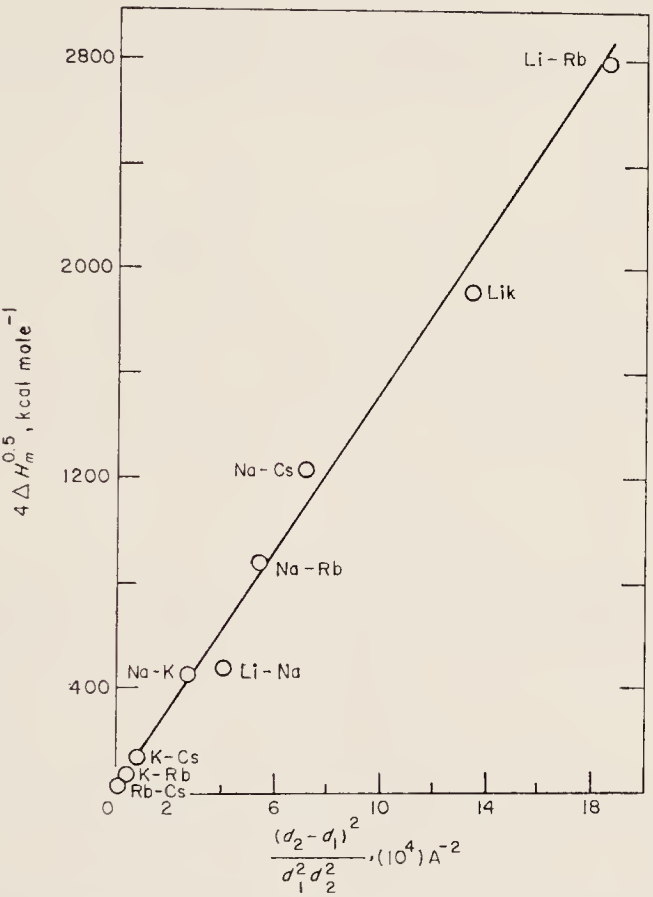

Fig. 2. Plot of $4\Delta H_m^{0.5}$ for the alkali nitrates versus the quantity $(d_2 - d_1)^2/(d_1 d_2)^2$. The cation pair to which each point corresponds is listed next to each point.

Equations (87)–(89) apply in aqueous solutions of two electrolytes in which the interaction potentials are conformal. For example, the assumptions utilized in the extensions of the Debye–Hückel theory (e.g. water is considered as a continuous dielectric medium of dielectric constant D, that the cation–anion repulsive potential is that of hard spheres, and that all the

other interionic interactions are coulombic) when combined with the Brönsted theory of specific ionic interactions make the system a special case of a conformal solution. Consequently, if the potentials are conformal, Eqs. (87)–(89) should apply to the thermodynamic excess functions for mixing two salts at constant ionic strength.

Measurements of ΔG_m^E have been obtained in the LiCl–NaCl and NaCl–KCl aqueous solutions for mixtures made from equal

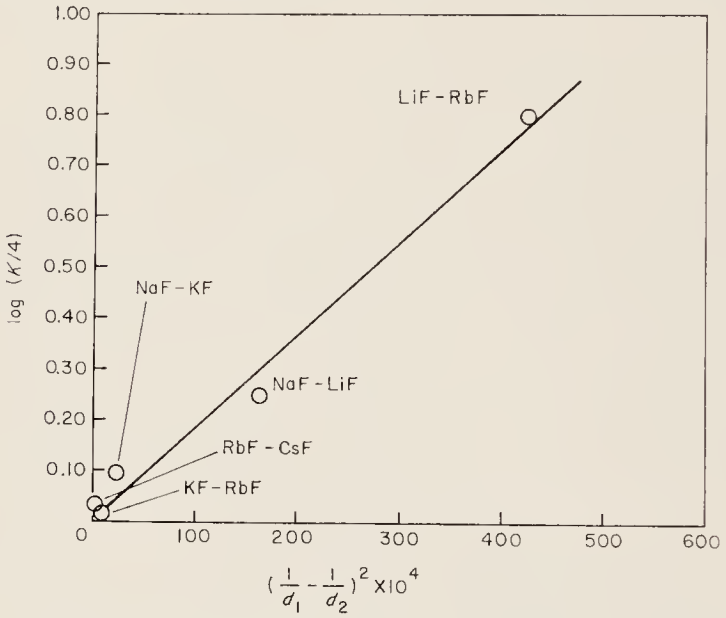

Fig. 3. Plot of the logarithm of the association constants for the exchange reaction $A_2X_2 + B_2X_2 \rightleftarrows 2\,ABX_2$ versus the function of the size parameters predicted by theory.

proportions of solutions of the two pure salts at the same ionic strength. The data do not conform to the functional dependence of the equations obtained from theory and do not even have the same sign. One may conclude that for these mixtures the pair interactions are not conformal and that the simple conformal potential functions ordinarily used in electrolyte theory do not adequately represent the interaction, perhaps because the interactions of the solvent cannot be considered as those of a continuous dielectric medium. Thus, the theory may be utilized to test assumptions in a proposed theory of aqueous electrolytes and in

this case indicates that the simple ionic potentials used in dilute solutions are inadequate to describe the concentrated ternary mixtures.

By arguments very similar to those used to derive Eqs. (87)–(89), one can show that the equilibrium constants for exchange reactions of ionic vapor dimer molecules

$$A_2X_2 + B_2X_2 \rightleftarrows 2\,ABX_2$$

have an equilibrium constant K of the form

$$\log (K/4) = R(g_1 - g_2)^2 + \ldots = S\left(\frac{1}{d_1} - \frac{1}{d_2}\right)^2 + \ldots \quad (91)$$

where R and S are constants which depend only on the comparison salt.[9] Figure 3 is a plot of $\log (K/4)$ versus $(1/d_1 - 1/d_2)^2$ for four alkali fluoride mixtures.[8] Within the uncertainties in the data the points lie on a single line. Further tests of Eq. (91) are desirable.

These examples are not meant to be exhaustive but merely illustrate the usefulness of the equations derived.

D. Reciprocal Systems[13]

Reciprocal molten salt systems are those containing at least two cations and two anions. We shall deal with the simplest member of this class, that containing the ions A^+, B^+, X^-, and Y^-. The four constituents of the solution, AX, BX, AY, and BY, will be designated by 1, 2, 3, and 4 respectively. There are four ions in the system and one restriction of electroneutrality. Consequently, of the four constituents, there are only three which are independent components. In order to calculate the Helmholtz free energy of mixing conveniently, we must (arbitrarily) choose the three components. Here we choose BX, AY, and BY. This choice requires that in order to make mixtures of some compositions a negative quantity of BY must be used. This presents no difficulty in the theory and is thermodynamically self-consistent. One mole of some arbitrary composition (X_A, X_B, X_X, X_Y) can be made by mixing X_X moles of BX (component 2), X_A moles of AY (component 3), and $(X_Y - X_A)$ moles of BY (component 4).*

* X_A and X_B are cation fractions and X_X and X_Y are anion fractions, e.g. $X_A = N_A/(N_A + N_B)$.

Thus the excess Helmholtz free energy of mixing may be calculated from the equation

$$\Delta A_m^E = A_m - X_X A_2 - X_A A_3 - (X_Y - X_A)A_4 - RT(X_A \ln X_A + X_B \ln X_B + X_X \ln X_X + X_Y \ln X_Y) \quad (92)$$

A_2, A_3, and A_4 are known from Eq. (79). A_m may be calculated from Eq. (54) and a modified form of Eq. (55)

$$Z_m = \frac{1}{N_A!N_B!N_X!N_Y!} \int \cdots \int \exp(-U_m/kT)(d\tau_a)^N(d\tau_c)^N = \frac{1}{N_A!N_B!N_X!N_Y!} Z'_m \quad (93)$$

where U_m in Eq. (93) is given by the expression

$$U_m = \sum_c^{X_A N} \sum_a^{X_X N} g_1 f(g_1 r) + \sum_c^{X_B N} \sum_a^{X_X N} g_2 f(g_2 r) + \sum_c^{X_A N} \sum_a^{X_Y N} g_3 f(g_3 r) + \sum_c^{X_B N} \sum_a^{X_Y N} g_4 f(g_4 r) + \sum_c^{N} \sum_a^{N} h(r) + \sum_{c<c'} \sum u' + \sum_{a<a'} \sum u'' \quad (94)$$

where the four perturbation parameters g_1, g_2, g_3, and g_4 are related because of the additivity of ionic radii

$$d_1 + d_4 = d_2 + d_3 \quad (95)$$

and

$$\frac{1}{g_1} + \frac{1}{g_4} = \frac{1}{g_2} + \frac{1}{g_3} \quad (96)$$

The calculations are given elsewhere[13] and are not repeated here since the method does not differ in principle from that for binary systems.

The result for the excess Helmholtz free energy of mixing leads to the equation

$$\frac{-\Delta A_m^E}{kT} = X_A X_X \frac{\mathbf{A}}{Z'_0}[(g_1 - 1) + (g_4 - 1) - (g_2 - 1) - (g_3 - 1)] + \tfrac{1}{2} X_A X_X \left[\frac{1}{Z'_0}(\mathbf{J} + N\mathbf{K} + N\mathbf{L} + N^2\mathbf{M}) - \left(\frac{\mathbf{A}}{Z'_0}\right)^2\right][(g_1 - 1)^2 + (g_4 - 1)^2$$

$$
\begin{aligned}
&- (g_2 - 1)^2 - (g_3 - 1)^2] \\
&+ \tfrac{1}{2} X_A X_B \left[\frac{1}{Z_0'}(N\mathbf{K} + N^2\mathbf{M}) - \left(\frac{\mathbf{A}}{Z_0'}\right)^2\right] \\
&\times [X_X(g_1 - g_2)^2 + X_Y(g_3 - g_4)^2] \\
&+ \tfrac{1}{2} X_X X_Y \left[\frac{1}{Z_0'}(N\mathbf{L} + N^2\mathbf{M}) - \left(\frac{\mathbf{A}}{Z_0'}\right)^2\right] \\
&\times [X_A(g_1 - g_3)^2 + X_B(g_2 - g_4)^2] \\
&+ \tfrac{1}{2} X_A X_B X_X X_Y \left[\frac{N^2}{Z_0'}\mathbf{M} - \left(\frac{\mathbf{A}}{Z_0'}\right)^2\right] \\
&\times (g_1 + g_4 - g_2 - g_3)^2 + \ldots
\end{aligned} \tag{97}
$$

It should be noted that first-order terms appear in Eq. (97). This is to be contrasted with binary systems where the first-order terms cancel. This equation can be simplified considerably. Comparison with Eq. (79) of the first two collections of terms in Eq. (97) having the coefficients $X_A X_X$ leads to the result (to second-order terms)

$$
\begin{aligned}
&X_A X_X(\mathbf{A}/Z_0')\,[(g_1 - 1) + (g_4 - 1) - (g_2 - 1) - (g_3 - 1)] \\
&\quad + \tfrac{1}{2} X_A X_X\,[(1/Z_0')\,(\mathbf{J} + N\mathbf{K} + N\mathbf{L} + N^2\mathbf{M}) - (\mathbf{A}/Z_0')^2] \\
&\quad \times [(g_1 - 1)^2 + (g_4 - 1)^2 - (g_2 - 1)^2 - (g_3 - 1)^2] \\
&\quad = X_A X_X(A_1 + A_4 - A_2 - A_3) = X_A X_X \Delta A^0
\end{aligned} \tag{98}
$$

where $\Delta A^0 = A_1 + A_4 - A_2 - A_3$ and is defined as the Helmholtz free energy change for the reaction

$$\mathrm{AY} + \mathrm{BX} \rightleftarrows \mathrm{AX} + \mathrm{BY} \tag{99}$$

Of the remaining second-order terms, the terms with the coefficient $X_A X_B X_X$ are exactly the same as those which occur in the binary system AX–BX multiplied by the ion fraction of X^-, X_X; the terms with the coefficient $X_A X_B X_Y$ are the same as for the system AY–BY multiplied by X_Y; and, similarly, the terms in $X_A X_X X_Y$ or $X_B X_X X_Y$ are the same as for the system AX–AY or BX–BY multiplied by the factors X_A or X_B respectively. These four collections of terms are the *linearly additive binary*

terms. Equation (98) can be rewritten as

$$\Delta A_m^E = X_A X_X \Delta A^\circ + X_X \Delta A_{12}^E + X_Y \Delta A_{34}^E + X_A \Delta A_{13}^E + X_B \Delta A_{24}^E + X_A X_B X_X X_Y \mathbf{P}(g_1 + g_4 - g_2 - g_3)^2 + \ldots \quad (100)$$

where **P** is a collection of constants dependent only on the properties of the "comparison" salt and ΔA_{ij}^E is the excess free energy of mixing of a binary mixture of the components i and j (ΔA_{12}^E is given by Eq. (87)), where AX = 1, BX = 2, AY = 3, and BY = 4.

The first five terms in Eq. (100) can be shown to be exact. For example, consider a "solution" consisting of the pure salt AX. In this solution $X_A = X_X = 1$. Since the ion fractions are unity the excess free energy of mixing is equal to the free energy change for making the solution (i.e. pure AX) from the three independent components AY, BX, and BY. This is accomplished by mixing 1 mole of AY, 1 mole of BX and −1 mole of BY, which is the reaction (99). Consequently, if the expression (100) were calculated exactly (i.e. including terms to all orders in $(g_i - 1)$ and for all kinds of interactions) all the terms containing the coefficients $X_A X_X$ only are equal to ΔA^0.* All other terms must contain X_B and/or X_Y and must approach zero as X_B and X_Y approach zero. The *linearly additive binary terms* may be shown to be exact to all orders in $(g_i - 1)$ and for all interactions by allowing either X_A, X_B, X_X, or X_Y to be zero. The equations reduce properly to the correct expressions for the binary systems not containing the A^+, B^+, X^-, or Y^- ions.

The first term in Eq. (100) may be calculated from the free energies of formation of pure salts and the four *linearly additive binary terms* may be evaluated from information on the four binary systems. Only the last term cannot be directly evaluated from information on lower-order systems. A useful approximation to **P** in this term may be made by comparing it with analogous terms in the quasi-lattice theory.[13,18] This approximation is

$$\mathbf{P}(g_1 + g_4 - g_2 - g_3)^2 = \frac{(\Delta A^0)^2}{2\mathbf{Z}RT} \quad (101)$$

* Terms in $X_A^n X_X^m$ which may appear in the result are assumed to be expanded as $X_A X_X (1 - X_B)^{n-1} (1 - X_Y)^{m-1} = X_A X_X (1 - \ldots)$.

where **Z** is a quasi-lattice coordination number. Using Eq. (101) to approximate the last term ($\mathbf{Z} = 5$) and experimental and tabulated data for the first five terms, calculations of activity coefficients of LiF from Eq. (100) were made and are compared with activity coefficients calculated from phase-diagram data

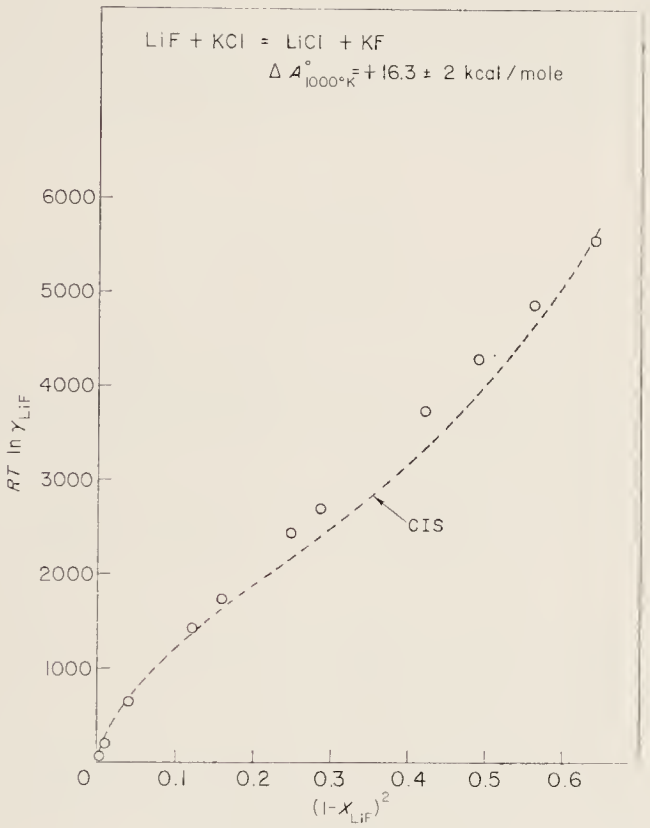

Fig. 4. Comparison of activity coefficients of LiF obtained from liquidus temperatures of LiF in the LiF–KCl system with those calculated from the conformal ionic solution theory (CIS).

on the LiF–KCl system in Fig. 4.[19] The agreement on magnitude and dependence upon concentration is excellent considering that no adjustable parameters were used. The last term in Eq. (100), which is equivalent to the second-order or "non-random mixing term" in the quasi-lattice theory, is significant and leads to the "S" shaped character of the curve.

V. CONCLUSIONS

Dimensional techniques provide a powerful tool for treating ionic systems and the comparisons made with data have been successful in demonstrating their value. Although there has been some recent work (e.g. Davis[20] has extended the theory to infinitely dilute solutions of two salts of two valence types), many other applications are possible. It is hoped that further experimental and theoretical work will amplify the uses of dimensional techniques and extend the work to systems which have not been examined.

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STATISTICAL MECHANICS OF MIXTURES— THE AVERAGE POTENTIAL MODEL

A. BELLEMANS, V. MATHOT and M. SIMON, *Faculty of Sciences, Université Libre de Bruxelles, Brussels, Belgium*

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I. INTRODUCTION

The extension of the cell model to multicomponent systems of spherical molecules of similar size, carried out initially by Prigogine and Garikian[1] in 1950 and subsequently continued by several authors,[2–5] was an important step in the development of the statistical theory of mixtures. Not only could the excess free energy be calculated from this model in terms of molecular interactions, but also all other excess properties such as enthalpy, entropy, and volume could be calculated, a goal which had not been reached before by the theories of regular solutions developed by Hildebrand and Scott[6] and Guggenheim.[7]

The greatest success of the cell model of solutions was probably the qualitative prediction that mixtures of spherical molecules of the same size may simultaneously show a positive excess free

energy and a negative excess volume:[2] examples of this behavior were reported for the first time by Mathot and Desmyter[8] (binary mixtures of CMe_4 with C_6H_6, CCl_4, and cyclohexane).

From the quantitative point of view, the success of the cell model of solutions was more limited. For example, a detailed analysis of the excess functions of seven binary mixtures by Prigogine and Bellemans[5] only showed a very rough agreement between theory and experiment. One should of course realize here that besides the use of the cell model itself, several supplementary assumptions had to be made in order to obtain numerical estimates of the excess functions. For example, it was assumed that two molecules of species α and β interact following the 6–12 potential of Lennard-Jones:

$$\varepsilon_{\alpha\beta}(r) = \varepsilon^*_{\alpha\beta}\left\{\left(\frac{r^*_{\alpha\beta}}{r}\right)^{12} - 2\left(\frac{r^*_{\alpha\beta}}{r}\right)^{6}\right\} \tag{1}$$

where r is their distance apart, and $r^*_{\alpha\beta}$, $-\varepsilon^*_{\alpha\beta}$ are the abscissa and ordinate of the minimum of $\varepsilon_{\alpha\beta}(r)$. This gives six characteristic parameters of interaction: ε^*_{AA}, ε^*_{AB}, ε^*_{BB}, r^*_{AA}, r^*_{AB}, r^*_{BB}, for a binary mixture A + B. As a consequence the behavior of the excess properties of such a mixture depends essentially on the four dimensionless parameters:

$$\delta = (\varepsilon^*_{BB} - \varepsilon^*_{AA})/\varepsilon^*_{AA} \tag{2}$$

$$\rho = (r^*_{BB} - r^*_{AA})/r^*_{AA} \tag{3}$$

$$\theta = (\varepsilon^*_{AB} - \tfrac{1}{2}\varepsilon^*_{AA} - \tfrac{1}{2}\varepsilon^*_{BB})/\varepsilon^*_{AA} \tag{4}$$

$$\sigma = (r^*_{AB} - \tfrac{1}{2}r^*_{AA} - \tfrac{1}{2}r^*_{BB})/r^*_{AA} \tag{5}$$

Two of them, δ and ρ, can be deduced from the properties of pure A and B by applying the *theorem of corresponding states* which is implied in assumption (1). The two other parameters, θ and σ, were eliminated by *assuming the combination rules*:

$$\varepsilon^*_{AB} = (\varepsilon^*_{AA}\varepsilon^*_{BB})^{\frac{1}{2}} \rightarrow \theta = \sqrt{1+\delta} - 1 - \tfrac{1}{2}\delta \tag{6}$$

$$r^*_{AB} = \tfrac{1}{2}(r^*_{AA} + r^*_{BB}) \rightarrow \sigma = 0 \tag{7}$$

There were thus many possibilities to account for the discrepancies observed by Prigogine and Bellemans;[5] three obvious ones are:

(a) all the mixtures listed are liquid at room temperature and involve therefore relatively complicated molecules which are not quite spherical and certainly deviate from Eq. (1);

(b) the cell model gives a rough account only of the thermodynamic properties of *pure* liquids so that one cannot expect that it will predict the properties of mixtures correctly;

(c) the questionable validity of the combination rules (6) and (7).

Point (a) shows the need of accurate data on mixtures of *simple molecules* (like argon, krypton, methane, etc., . . .) in order to test the theory significantly. The first careful study of such a system (CO–CH_4 at 90.7°K) was performed by Mathot, Staveley, *et al.* in 1956;[9] it was followed by many similar studies of other *simple mixtures* so that we presently have a good deal of experimental information about such systems.

Concerning point (b), a generalized theory was developed independently by Prigogine and his co-workers[10,11] and by Scott.[12] The main idea was to combine the concept of *average potential* involved in the cell model with the *theorem of corresponding states* for pure compounds, in such a way that:

(a) for pure substances this new theory of solutions reduces exactly to the theorem of corresponding states which (contrary to the cell model) rests upon very general assumptions and is quite well verified by *simple liquids*;

(b) the excess properties of mixtures can be expressed in terms of (i) the experimental properties of a pure component taken as reference and (ii) the molecular parameters δ, ρ, θ, σ introduced previously.

On account of its underlying assumptions this model has alternatively been called the *Average Potential Model* (APM)[11] or the *Corresponding States Theory of Mixtures*.[12] Various slightly different versions of it have been developed, depending on the precise definition of the average potential acting on a molecule;[11,12] extensions and comments on this model have been published by several authors.[13–16]

The predictions of the APM were compared by Prigogine in

1957 with the limited data available at that time for simple mixtures;[11] in order to do this, the theoretical excess functions were expanded in δ, ρ, and θ up to second powers,* the coefficients of these expansions being expressed in terms of the thermodynamic properties of the reference substance. The agreement with the experimental data looked somewhat better than for the cell model but the essential conclusions were that:

(a) very accurate data are needed for the reference substance;

(b) the excess properties are extremely sensitive to the values of both the parameters δ and ρ (θ and σ being eliminated through the combination rules (6)–(7));

(c) the expansions of the excess functions in powers of δ, ρ, and θ up to second-order terms are in most cases inadequate for a quantitative discussion because of their slow convergence.

Recently the applicability of the APM has been reinvestigated by Staveley and his co-workers[17,18] and by Knobler *et al.*[19] in relation to the latest experimental data available on simple mixtures, with rather discouraging results. It actually seems to us that the analysis of these authors neither validates nor invalidates the APM itself but rather shows how difficult it is to use the model efficiently for practical calculations on account of points (a), (b), and (c) listed above.

A great many of the difficulties (and sometimes the misunderstandings) arise from point (c). It is however important to notice that the APM describes the properties of solutions as finite differences between suitable composition-dependent averages and the properties of the pure components. Series expansions in powers of δ, ρ, θ, and σ were introduced *afterwards* for the purpose of qualitative discussion and comparison with other treatments, e.g., the theory of conformal solutions.[34,35,36] They introduce artificial difficulties due to their slow convergence† which have nothing to do with the physical ideas of the APM. Therefore expansions of this type should be proscribed for all quantitative applications; one should instead use the compact expressions of the excess functions.

* σ was set equal to zero from the beginning in accordance with the combination rule (7).

† For example, the calculated excess properties depend on which component A or B is selected as reference.

The purpose of the present paper is mainly to give a detailed and *significant* comparison of the APM with the presently available experimental data on simple mixtures. With this purpose in mind we shall:

(i) select the most likely appropriate and *most tractable* version of the APM among the various available ones;

(ii) avoid expanded forms of the excess functions in powers of δ, ρ, θ, and σ but instead use their full expressions (as given in Ref. 11); such a method escapes the criticism (c) and has been previously developed by two of us;[20]

(iii) select a series of pure substances which verify the theorem of corresponding states closely, and fit their reduced properties by appropriate analytical forms which will next be used to calculate the excess functions;

(iv) select the values of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA} (i.e., δ and ρ) very carefully for each mixture and eventually inquire about the validity of the combination rules (6) and (7). These various points will be treated in Sections II, III, and IV.

The comparison with the experimental data will then be made in Sections V and VI:

(a) in Section V we shall discuss the *qualitative* behavior of the main excess functions versus δ and ρ (assuming the validity of the combination rules);

(b) in Section VI we shall focus on five selected systems, the main excess functions of which are accurately known, and see how far a *quantitative* agreement can be obtained (by eventually giving up the combination rules).

Final conclusions and comments will be drawn in Section VII.

II. THE VARIOUS VERSIONS OF THE AVERAGE POTENTIAL MODEL

The APM relies essentially on two bases. The first one is the *theorem of corresponding states* which says that the configurational partition function of a classical assembly of N molecules may be written in the form:

$$Q(N, T, V) = r^{*3N} q(\tilde{T}, \tilde{v})^N \tag{8}$$

provided that the interaction energy between the molecules is the sum of central two-body potentials:

$$\varepsilon(r) = \varepsilon^* \varphi(r/r^*) \tag{9}$$

where φ is a universal function, r is the distance between two molecules, and r^*, $-\varepsilon^*$ are the abcissa and ordinate of the mini-

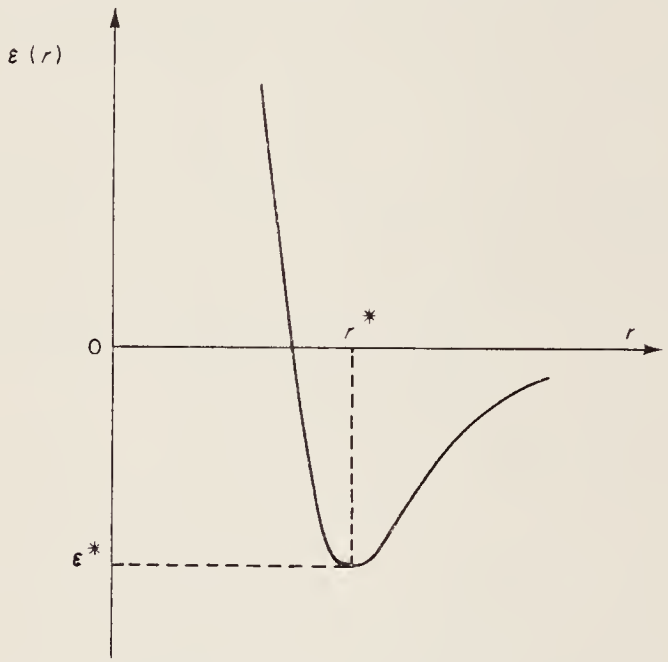

Fig. 1. Schematic representation of the pair potential $\varepsilon(r)$.

mum of $\varepsilon(r)$ (see Fig. 1). $\tilde{T}$ and $\tilde{v}$ are the reduced temperature and volume (per molecule):

$$\tilde{T} = kT/\varepsilon^*, \qquad \tilde{v} = V/Nr^{*3} \tag{10}$$

and $q(\tilde{T}, \tilde{v})$ is a universal function (partition function per molecule of the system) from which the configurational Helmholtz free energy is obtained:

$$\begin{aligned} F_{\text{conf.}}/NkT &= -\ln q(\tilde{T}, \tilde{v}) - 3 \ln r^* \\ &\equiv \xi(\tilde{T}, \tilde{v}) - 3 \ln r^* \end{aligned} \tag{11}$$

with $\xi = -\ln q$. The pressure p in the system is then given as:

$$pr^{*3}/kT = \tilde{p}/\tilde{T} = -\partial\xi(\tilde{T}, \tilde{v})/\partial\tilde{v} \tag{12}$$

where $\tilde{p}$ is the reduced pressure

$$\tilde{p} = pr^{*3}/\varepsilon^* \tag{13}$$

The Gibbs free energy is obtained by combining Eqs. (11) and (12) and eliminating $\tilde{v}$ in terms of $\tilde{p}$ and $\tilde{T}$:

$$\begin{aligned} G_{\text{conf.}}/NkT &= \xi(\tilde{T}, \tilde{v}) + \tilde{p}\tilde{v}/\tilde{T} - 3 \ln r^* \\ &= \xi(\tilde{T}, \tilde{v}) - \tilde{v}\partial\xi(\tilde{T}, \tilde{v})/\partial\tilde{v} - 3 \ln r^* \\ &\equiv \eta(\tilde{T}, \tilde{p}) - 3 \ln r^* \end{aligned} \tag{14}$$

with $\eta = \xi - \tilde{v}\partial\xi/\partial\tilde{v}$. The functions $\xi(\tilde{T}, \tilde{v})$ and $\eta(\tilde{T}, \tilde{p})$ can be constructed from the experimental data of pure substances which satisfy the theorem of corresponding states.[20]

The second basis of the APM is the *cell model*, which is required in order to define the average potential acting on a molecule in a mixture A + B. The particular way this average potential is constructed from the pair potentials $\varepsilon_{AA}(r)$, $\varepsilon_{AB}(r)$, and $\varepsilon_{BB}(r)$ leads to the different versions of the APM.

(a) Crude version

One assumes that a mixture A + B with mole fractions x_A, x_B behaves like a pure component with the average two-body potential:

$$\langle \varepsilon(r) \rangle = x_A^2 \varepsilon_{AA}(r) + 2x_A x_B \varepsilon_{AB}(r) + x_B^2 \varepsilon_{BB}(r) \tag{15}$$

It is assumed further that (i) $\varepsilon_{AA}(r)$, $\varepsilon_{AB}(r)$, and $\varepsilon_{BB}(r)$ conform to Eq. (9) and (ii) the analytic form of φ is such that $\langle \varepsilon(r) \rangle$ itself conforms to Eq. (9):

$$\langle \varepsilon(r) \rangle = \langle \varepsilon^* \rangle \varphi(r/\langle r^* \rangle) \tag{16}$$

where $\langle \varepsilon^* \rangle$ and $\langle r^* \rangle$ are functions of $\varepsilon^*_{\alpha\beta}$, $r^*_{\alpha\beta}$ ($\alpha, \beta = A, B$) and of the mole fractions.

Assumption (ii) is by no means a trivial one since it limits φ to the Lennard-Jones form[14]

$$\varphi(r/r^*) = \frac{n}{m-n}\left(\frac{r^*}{r}\right)^m - \frac{m}{m-n}\left(\frac{r^*}{r}\right)^n \tag{17}$$

($m > n$). In what follows we shall always use the common values $m = 12$, $n = 6$ (except in Section VII where we briefly discuss

the influence of the choice of the m, n values upon the excess functions). We have then

$$\langle \varepsilon^* \rangle = \frac{[x_A^2 \varepsilon_{AA}^* r_{AA}^{*6} + 2x_A x_B \varepsilon_{AB}^* r_{AB}^{*6} + x_B^2 \varepsilon_{BB}^* r_{BB}^{*6}]^2}{[x_A^2 \varepsilon_{AA}^* r_{AA}^{*12} + 2x_A x_B \varepsilon_{AB}^* r_{AB}^{*12} + x_B^2 \varepsilon_{BB}^* r_{BB}^{*12}]} \tag{18}$$

$$\langle r^* \rangle = \left[\frac{x_A^2 \varepsilon_{AA}^* r_{AA}^{*12} + 2x_A x_B \varepsilon_{AB}^* r_{AB}^{*12} + x_B^2 \varepsilon_{BB}^* r_{BB}^{*12}}{x_A^2 \varepsilon_{AA}^* r_{AA}^{*6} + 2x_A x_B \varepsilon_{AB}^* r_{AB}^{*6} + x_B^2 \varepsilon_{BB}^* r_{BB}^{*6}} \right]^{\frac{1}{6}} \tag{19}$$

Within the present approximation the partition function of the mixture has the same structure (8) as a pure component, except for the ideal combinatorial factor:

$$Q(N_A, N_B, V, T) = \frac{N!}{N_A! N_B!} \langle r^* \rangle^{3N} q(\langle \tilde{T} \rangle, \langle \tilde{v} \rangle) \tag{20}$$

with

$$\langle \tilde{T} \rangle = kT/\langle \varepsilon^* \rangle, \qquad \langle \tilde{v} \rangle = V/N\langle r^* \rangle^3 \tag{21}$$
$$N = N_A + N_B$$

(*b*) *Refined versions*

The obvious refinement is to consider two distinct average potentials for molecules A and B in their respective surroundings:

$$\langle \varepsilon_A(r) \rangle = x_A \varepsilon_{AA}(r) + x_B \varepsilon_{AB}(r) \tag{22}$$

$$\langle \varepsilon_B(r) \rangle = x_A \varepsilon_{AB}(r) + x_B \varepsilon_{BB}(r) \tag{23}$$

Keeping assumptions (i) and (ii) introduced above in (a) one has:

$$\langle \varepsilon_A(r) \rangle = \langle \varepsilon_A^* \rangle \varphi(r/\langle r_A^* \rangle) \tag{24}$$

$$\langle \varepsilon_B(r) \rangle = \langle \varepsilon_B^* \rangle \varphi(r/\langle r_B^* \rangle) \tag{25}$$

with (for a 6–12 potential):

$$\langle \varepsilon_A^* \rangle = \frac{[x_A \varepsilon_{AA}^* r_{AA}^{*6} + x_B \varepsilon_{AB}^* r_{AB}^{*6}]^2}{[x_A \varepsilon_{AA}^* r_{AA}^{*12} + x_B \varepsilon_{AB}^* r_{AB}^{*12}]} \tag{26}$$

$$\langle r_A^* \rangle = \left[\frac{x_A \varepsilon_{AA}^* r_{AA}^{*12} + x_B \varepsilon_{AB}^* r_{AB}^{*12}}{x_A \varepsilon_{AA}^* r_{AA}^{*6} + x_B \varepsilon_{AB}^* r_{AB}^{*6}} \right]^{\frac{1}{6}} \tag{27}$$

(and similar expressions for $\langle \varepsilon_B^* \rangle$, $\langle r_B^* \rangle$).

One assumes next that the partition functions of molecules A and B in their respective average surroundings are:

$$\langle r_A^* \rangle^3 q(\langle \tilde{T}_A \rangle, \langle \tilde{v}_A \rangle) \quad \text{and} \quad \langle r_B^* \rangle^3 q(\langle \tilde{T}_B \rangle, \langle \tilde{v}_B \rangle)$$

and that the total partition function of the mixture is:

$$Q(N_A, N_B, V, T) = \frac{N!}{N_A! N_B!} \langle r_A^* \rangle^{3N_A} q(\langle \tilde{T}_A \rangle, \langle \tilde{v}_A \rangle)^{N_A} \times \langle r_B^* \rangle^{3N_B} q(\langle \tilde{T}_B \rangle, \langle \tilde{v}_B \rangle)^{N_B} \quad (28)$$

with

$$\langle \tilde{T}_A \rangle = kT/\langle \varepsilon_A^* \rangle, \qquad \langle \tilde{T}_B \rangle = kT/\langle \varepsilon_B^* \rangle \quad (29)$$

$$V = N_A \langle r_A^* \rangle^3 \langle \tilde{v}_A \rangle + N_B \langle r_B^* \rangle^3 \langle \tilde{v}_B \rangle \quad (30)$$

All these expressions clearly reduce to the theorem of corresponding states for a one-component system (cf. Eqs. (8) and (10)). The problem is now to attribute values to the reduced volumes $\langle v_A \rangle$ and $\langle v_B \rangle$ for A and B molecules in their respective mean fields; in other words how is the available volume V shared between the molecules A and B? We recover here a typical problem of the cell model. Three different assumptions on $\langle \tilde{v}_A \rangle$, $\langle \tilde{v}_B \rangle$ have been proposed[11] leading to slightly different versions of the APM:

(I) V is shared equally between the N molecules,

$$\langle \tilde{v}_A \rangle \langle r_A^* \rangle^3 = \langle \tilde{v}_B \rangle \langle r_B^* \rangle^3 = V/N \quad (31)$$

(II) V is shared unequally between A and B molecules by minimizing the free energy of the system with respect to $\langle \tilde{v}_A \rangle$ and $\langle \tilde{v}_B \rangle$ subject to the restriction (30):

(III) V is shared unequally between A and B molecule by assuming that the available volumes for an A and a B molecule are in the ratio $\langle r_A^* \rangle^3 / \langle r_B^* \rangle^3$, i.e.,

$$\langle \tilde{v}_A \rangle = \langle \tilde{v}_B \rangle \quad (32)$$

We have so far four different versions of the APM: the *crude version* and the *refined versions* I, II, and III. Their common features are obviously that their partition functions (i) reduce to the exact form (8) for a one-component system, and (ii) depend on the function $q(\tilde{T}, \tilde{v})$ alone.

The thermodynamic excess functions of these four versions of the APM have been investigated by Prigogine and his coworkers[10,11] and it turns out that nearly equivalent results are respectively found for (a) the *crude version* and the *refined version I* (which both assume an equal sharing of V between the molecules),

and (b) the *refined version II* and the *refined version III* (unequal sharing of V). It therefore seems natural to retain only two versions, one of class (a) and one of class (b), and to select them following the criterion of *simplicity*.

In this respect it must be recalled[11] that all thermodynamic properties deduced from the *crude version* and the *refined version II* depend on the function $\eta(\tilde{T}, \tilde{p})$ while for the other two versions it is the function $\xi(\tilde{T}, \tilde{v})$ which is needed. As the thermodynamic properties of mixtures are usually measured in such conditions that T and p are independent variables (often with $p \simeq 0$), it is obviously easier to work with models involving $\eta(\tilde{T}, \tilde{p})$ rather than $\xi(\tilde{T}, \tilde{v})$. We shall therefore limit ourselves from now on to the *crude version* and the *refined version II*. Their Gibbs configurational free energies are respectively:[21]

$$\frac{G_{\text{conf.}}}{NkT} = \eta(\langle\tilde{T}\rangle, \langle\tilde{p}\rangle) - 3 \ln \langle r^* \rangle + x_A \ln x_A + x_B \ln x_B \quad (33)$$

and

$$\frac{G_{\text{conf.}}}{NkT} = x_A \eta(\langle\tilde{T}_A\rangle, \langle\tilde{p}_A\rangle) + x_B \eta(\langle\tilde{T}_B\rangle, \langle\tilde{p}_B\rangle) - 3[x_A \ln \langle r_A^* \rangle + x_B \ln \langle r_B^* \rangle] + x_A \ln x_A + x_B \ln x_B \quad (34)$$

$\langle\tilde{p}_A\rangle$ and $\langle\tilde{p}_B\rangle$ are reduced pressures defined as:

$$\langle\tilde{p}_A\rangle \langle\varepsilon_A^*\rangle / \langle r_A^{*3}\rangle = \langle\tilde{p}_B\rangle \langle\varepsilon_B^*\rangle / \langle r_B^{*3}\rangle = p \quad (35)$$

The main excess properties are the free energy g^E, enthalpy h^E, entropy s^E, and volume v^E (per molecule); data on other excess properties (specific heat, thermal expansion or compressibility) are rather scarce. In most cases g^E, h^E, s^E, and v^E have been determined at low pressures ($\leqslant$1 atm) so that for practical calculations p may be equated to zero; their theoretical expressions deduced from Eqs. (33) and (34) are then as follows:

(*a*) *Crude version*

$$g^E/kT = \eta_0(\langle\tilde{T}\rangle) - x_A \eta_0(\tilde{T}_{AA}) - x_B \eta_0(\tilde{T}_{BB}) - 3\{\ln \langle r^* \rangle - x_A \ln r_{AA}^* - x_B \ln r_{BB}^*\} \quad (36)$$

$$v^E = \langle r^* \rangle^3 \omega(\langle\tilde{T}\rangle) - x_A r_{AA}^{*3} \omega(\tilde{T}_{AA}) - x_B r_{BB}^{*3} \omega(\tilde{T}_{BB}) \quad (37)$$

(*b*) *Refined version*

$$g^E/kT = x_A[\eta_0(\langle \tilde{T}_A \rangle) - \eta_0(\tilde{T}_{AA})] + x_B[\eta_0(\langle \tilde{T}_B \rangle) - \eta_0(\tilde{T}_{BB})] - 3[x_A \ln (\langle r_A^* \rangle / r_{AA}^*) + x_B \ln (\langle r_B^* \rangle / r_{BB}^*)] \quad (38)$$

$$v^E = x_A[\langle r_A^* \rangle^3 \omega(\langle \tilde{T}_A \rangle) - r_{AA}^{*3} \omega(\tilde{T}_{AA})] + x_B[\langle r_B^* \rangle^3 \omega(\langle \tilde{T}_B \rangle) - r_{BB}^{*3} \omega(\tilde{T}_{BB})] \quad (39)$$

The functions $\eta_0(\tilde{T})$ and $\omega(\tilde{T})$ are defined as:

$$\eta_0(\tilde{T}) = \eta(\tilde{T}, 0) \quad (40a)$$

$$\omega(\tilde{T}) = \tilde{T} \left(\frac{\partial}{\partial \tilde{p}} \eta(\tilde{T}, \tilde{p}) \right)_{p=0} \quad (40b)$$

$\omega(\tilde{T})$ is simply the reduced volume of a pure component extrapolated to $p = 0$.

Explicit formulas for h^E and s^E will not be quoted here: they are readily deduced from Eqs. (36) and (38) through the relationships:

$$h^E = \frac{\partial(g^E/T)}{\partial(1/T)}, \qquad s^E = \frac{h^E - g^E}{T} \quad (41)$$

Hence it appears that a knowledge of two functions only, $\eta_0(\tilde{T})$ and $\omega(\tilde{T})$, is required to compute g^E, h^E, s^E, and v^E at $p = 0$. (Note that the excess specific heat c^E and the thermal expansion dv^E/dT may also be computed from these functions.)

III. ANALYTICAL EXPRESSIONS FOR $\eta_0(\tilde{T})$ AND $\omega(T)$

The functions $\eta_0(\tilde{T})$ and $\omega(\tilde{T})$ have been obtained from the experimental data of selected substances which closely follow the theorem of corresponding states.[20] Six substances were retained: argon, krypton, xenon, methane, carbon monoxide, and nitrogen (neon was discarded on account of quantum translational effects).

In order to put the experimental thermodynamic properties of these substances in reduced units, their values ε^* and r^* were needed and the convention was made to deduce them from the experimental critical temperatures and pressures through the corresponding relationships:

$$kT_{\text{crit.}} = \alpha\varepsilon^*, \qquad kT_{\text{crit.}}/p_{\text{crit.}} = \gamma r^{*3} \quad (42)$$

(We disregarded the critical volumes, which are generally less accurate.) The following values were assigned to the proportionality constants in Eq. (42):

$$\alpha = 1.224, \qquad \gamma = 7.960 \tag{43}$$

with the convention that for krypton:

$$\varepsilon^*/k = 171°\mathrm{K}, \qquad r^* = 4.04\ \mathrm{A} \tag{44}$$

these last values being obtained from accurate second virial coefficient measurements.[22] The experimental values of $T_{\mathrm{crit.}}$, $p_{\mathrm{crit.}}$ and the calculated values of ε^*, r^{*3} are listed in Table I for the six substances Kr, A, Xe, CO, N_2, and CH_4.

TABLE I. Values of ε^* and r^{*3} for Kr, A, Xe, CO, N_2, and CH_4, Deduced from $T_{\mathrm{crit.}}$ and $p_{\mathrm{crit.}}$ with Kr as Reference (N_a = Avogadro's number)

	$T_{\mathrm{crit.}}$, °K	$p_{\mathrm{crit.}}$, atm	ε^*/k, °K	r^{*3}, A^3	$N_a r^{*3}$, cm^3
Kr	209.4	54.3	171	66.0	39.7
A	151.0	48.0	123.2	53.8	32.4
Xe	289.8	58.0	236.6	85.5	51.5
CO	133.0	34.5	108.6	66.0	39.7
N_2	126.2	33.5	103.0	64.5	38.8
CH_4	191.1	45.8	156.0	71.4	43.0

We shall now briefly explain how the functions $\eta_0(\tilde{T})$ and $\omega(\tilde{T})$ were constructed. A detailed account of this question has been published elsewhere[20] (including a full list of references for the experimental data which were used).

Construction of $\omega(\tilde{T})$

The experimental liquid volumes of the pure substances versus T are reduced with the aid of the ε^*, r^* values of Table I (usually these volumes were measured under saturated pressure and they had first to be extrapolated to $p = 0$). The reduced experimental molecular volumes of A, Kr, CO, N_2, and CH_4 were plotted

in Fig. 2 as functions of $\tilde{T}$; therefrom the following analytical expression for $\omega(\tilde{T})$ was calculated by the method of least squares:

$$\omega(\tilde{T}) = 0.952596 - 0.705204\tilde{T} + 0.834608\tilde{T}^2 \qquad (45)$$

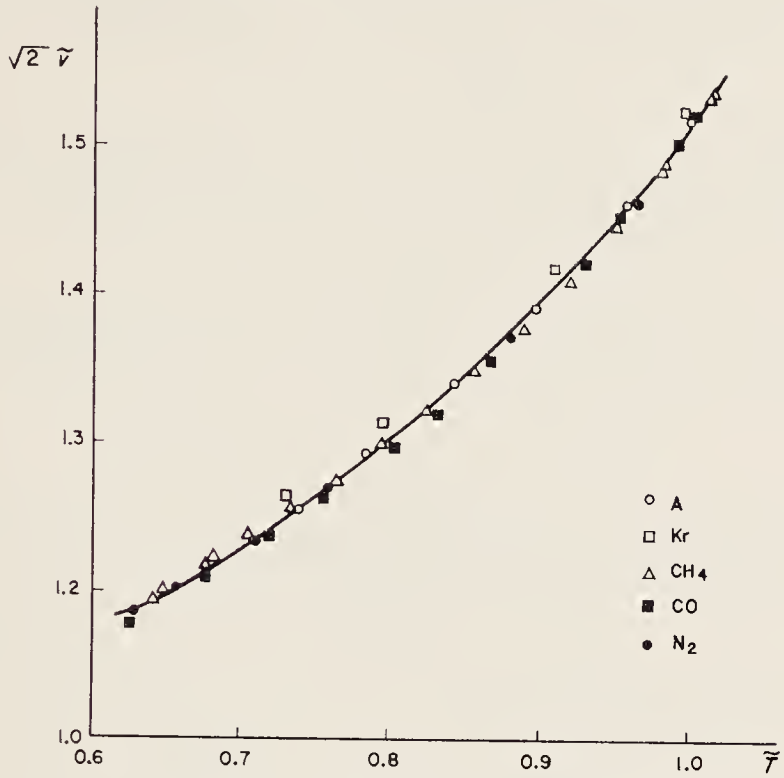

Fig. 2. Verification of the theorem of corresponding states.
The reduced volume $\tilde{v}$ as a function of $\tilde{T}$.
Plain curve: Eq. (45) times $\sqrt{2}$.

Construction of $\eta_0(\tilde{T})$

From Eq. (14) we have the following link between $\eta(\tilde{T}, \tilde{p})$ and the chemical potential $\mu_{\text{conf.}}$:

$$\eta(\tilde{T}, \tilde{p}) = \mu_{\text{conf.}}/kT + 3 \ln r^* \qquad (46)$$

Similar relations are obtained by successive differentiations of $\eta(\tilde{T}, \tilde{p})$ with respect to $\tilde{T}$:

$$-\tilde{T}\frac{\partial \eta}{\partial \tilde{T}} = h_{\text{conf.}}/kT \qquad (47)$$

$$-\frac{\partial}{\partial \tilde{T}}\left(\tilde{T}^2 \frac{\partial \eta}{\partial \tilde{T}}\right) = c_{\text{conf.}}/k \qquad (48)$$

where $h_{\text{conf.}}$ and $c_{\text{conf.}}$ are respectively the configurational enthalpy and specific heat at constant p per molecule. The values of $\mu_{\text{conf.}}$, $h_{\text{conf.}}$, and $c_{\text{conf.}}$ in the liquid range can be obtained experimentally as follows:

(a) One has along the liquid–vapor coexistence line:

$$\mu_{\text{conf.}}(\text{liq.}) = \mu_{\text{conf.}}(\text{gas}) \tag{49}$$

$\mu_{\text{conf.}}(\text{gas})$ can be obtained from the vapor pressure data versus T, plus the required corrections for gas imperfections:

$$\mu_{\text{conf.}}(\text{gas}) = kT \ln\left(\frac{p}{kT}\right) + Bp + \frac{C - B^2}{2kT} p^2 \tag{50}$$

where B, C are the second and third virial coefficients; finally $\mu_{\text{conf.}}(\text{liq.})$ extrapolated to zero pressure is given by:

$$\mu_{\text{conf.}}(\text{liq.})_{p=0} = \mu_{\text{conf.}}(\text{gas})_p - \int_0^p v(\text{liq.})\, dp \tag{51}$$

(b) Similarly the configurational enthalpy of the liquid can be deduced from the heats of vaporization, indeed:

$$h_{\text{conf.}}(\text{liq.}) - h_{\text{conf.}}(\text{gas}) = -h_{\text{vap.}} \tag{52}$$

$h_{\text{conf.}}(\text{gas})$ is evaluated from the second (and eventually the third) virial coefficient:

$$h_{\text{conf.}}(\text{gas}) = kT + \left(B - T\frac{dB}{dT}\right) p \tag{53}$$

so that $h_{\text{conf.}}(\text{liq.})$ extrapolated to zero pressure is given by:

$$h_{\text{conf.}}(\text{liq.})_{p=0} = -h_{\text{vap.}} - h_{\text{conf.}}(\text{gas})_p - \int_0^p \left(v - T\frac{dv}{dT}\right)_{\text{liq.}} dp \tag{54}$$

(c) Finally the configurational specific heat of the liquid is given by

$$c_{\text{conf.}}(\text{liq.}) = c_p(\text{liq.}) - c_v(\text{ideal gas}) \tag{55}$$

(with due extrapolations to $p = 0$); c_p and c_v are respectively the specific heats at constant pressure and volume.

The following analytical form was assumed:

$$\eta_0(\tilde{T}) = a/\tilde{T} + b \ln \tilde{T} + c\tilde{T} + f\tilde{T}^2 + d \tag{56}$$

and the five coefficients a, b, c, d, and f were adjusted by the method of least squares in order to fit as well as possible the three sets of data (a), (b), and (c) simultaneously for A, Kr, Xe, CO, N_2, and CH_4. This led to the following expression:

$$\eta_0(\tilde{T}) = -8.379308/\tilde{T} - 4.597179 \ln \tilde{T} + 2.301041\tilde{T} - 0.806469\tilde{T}^2 + 3.558774 \quad (57)$$

IV. DETERMINATION OF THE PARAMETERS OF INTERACTION FOR MIXTURES. DISCUSSION OF THE COMBINATION RULES

In order to calculate explicitly the excess properties of a mixture A + B from the formulas of Section II, we need the values of the six quantities:

$$\varepsilon^*_{AA}, \varepsilon^*_{AB}, \varepsilon^*_{BB} \quad \text{and} \quad r^*_{AA}, r^*_{AB}, r^*_{BB} \quad (58)$$

which are involved in the parameters $\langle\varepsilon^*\rangle$, $\langle r^*\rangle$, and $\langle\varepsilon^*_A\rangle$, $\langle\varepsilon^*_B\rangle$, $\langle r^*_A\rangle$, $\langle r^*_B\rangle$ characterizing the average potential; cf. Eqs. (18)–(19) and (26)–(27). Equivalently instead of considering the six quantities (58) we may use ε^*_{AA}, r^*_{AA}, and the four (dimensionless) ratios:

$$\varepsilon^*_{BB}/\varepsilon^*_{AA} = 1 + \delta, \qquad r^*_{BB}/r^*_{AA} = 1 + \rho \quad (59)$$

$$(\varepsilon^*_{AB} - \tfrac{1}{2}\varepsilon^*_{AA} - \tfrac{1}{2}\varepsilon^*_{BB})/\varepsilon^*_{AA} = \theta, \qquad (r^*_{AB} - \tfrac{1}{2}r^*_{AA} - \tfrac{1}{2}r^*_{BB})/r^*_{AA} = \sigma \quad (60)$$

It has been stressed in Section I that it is essentially these four parameters δ, ρ, θ, and σ which determine the values of the excess properties of the mixture A + B: should all these parameters be equal to zero then all excess functions vanish.

In the following sections we shall discuss some of the excess properties of the following mixtures:

$$CO\text{–}CH_4,\ A\text{–}CH_4,\ A\text{–}O_2,\ N_2\text{–}O_2,$$
$$N_2\text{–}A,\ CH_4\text{–}Kr,\ CO\text{–}N_2 \text{ and } CO\text{–}A;$$

we therefore need to know their molecular parameters (58) accurately.

In each mixture any one of the two components (say A) can be selected as reference substance and its corresponding values

ε^*_{AA}, r^*_{AA} taken from Table I. The problem is then to find the values of δ, ρ, and σ.

The two parameters δ and ρ for a given pair of substances can be obtained by application of the theorem of corresponding states to any suitable thermodynamic property. For example, in Section III we used the critical temperatures and pressures to determine the values of ε^* and r^* for a series of substances, Kr being taken as reference. Of course all ratios of ε^* and r^* for two substances, obtained from different thermodynamic properties, should agree closely: the contrary would mean that the theorem of corresponding states is badly violated.

The analytic expressions of the functions $\omega(\tilde{T})$ and $\eta_0(\tilde{T})$ reported in Section III were obtained from a reduction of the experimental data of various substances based on values of ε^* and r^* deduced from critical temperatures and pressures only:[20] as all the experimental points fell reasonably close to a mean curve (cf. Fig. 2), both functions $\omega(\tilde{T})$ and $\eta_0(\tilde{T})$ were quite accurately determined in this way. Here of course the reduction involved the knowledge of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA} for several substances.

The situation is quite different for the excess properties of one particular mixture A + B, where it is now $\delta = (\varepsilon^*_{BB}/\varepsilon^*_{AA}) - 1$ and $\rho = (r^*_{BB}/r^*_{AA}) - 1$ which are required (and not simply $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA}): it is essential here to get values which are as accurate as possible for these quantities. We shall therefore deduce δ and ρ (or alternatively $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA}) from different source data, see how far these values agree with each other, and finally select from them an average value. The following experimental data were used:

(a) the critical temperatures and pressures:

$$\varepsilon^*_{BB}/\varepsilon^*_{AA} = T^B_{crit.}/T^A_{crit.} \tag{61}$$

$$r^*_{BB}/r^*_{AA} = (T^B_{crit.}p^A_{crit.}/T^A_{crit.}p^B_{crit.})^{\frac{1}{3}} \tag{62}$$

(b) values of ε^* and r^* deduced from measurements of the second virial coefficient vs. T;

(c) values of ε^* and r^* deduced from experimental data on the viscosities of gases.*

* Note that (b) and (c) are slightly less general than (a) because the assumption of a 6–12 potential is explicitly used in deriving numerical values for ε^* and r^*.

The values of the ratios $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA} obtained by these three methods for a series of simple substances (argon being taken as reference) are respectively quoted in Tables II, III, and IV, and subsequently compared with each other in Tables V and VI.

From Table V we see that in general the values of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ deduced from critical constants and second virial coefficients agree rather well with each other while there seems to be a large discrepancy with the values obtained from viscosity. This tends

TABLE II. Values of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA}, Deduced from Critical Temperatures and Pressures (argon taken as reference)

	$T_{crit.}$, °K,	$p_{crit.}$, atm	$\varepsilon^*_{BB}/\varepsilon^*_{AA}$	r^*_{BB}/r^*_{AA}
A	151	48.0	1	1
Kr	209.4	54.3	1.387	1.070
N_2	126.2	33.5	0.836	1.062
O_2	154.4	49.7	1.022	0.996
CO	133	34.5	0.881	1.070
CH_4	191.1	45.8	1.226	1.099

TABLE III. Values of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA}, Deduced from ε^* and r^* Values from Second Virial Coefficients (argon taken as reference). Experimental sources: see Hirschfelder, Curtiss, and Bird[23]

	ε^*/k, °K	$r^* 2^{-\frac{1}{6}}$, A	$\varepsilon^*_{BB}/\varepsilon^*_{AA}$	r^*_{BB}/r^*_{AA}
A	119.8 122	3.405 3.40	1	1
Kr	171 158	3.60 3.597	1.361	1.058
N_2	95.05 95.9	3.698 3.71	0.790	1.089
O_2	117.5 118	3.58 3.46	0.974	1.035
CO	100.2	3.763	0.829	1.106
CH_4	148.2	3.817	1.226	1.122

to indicate that the ε^*'s determined from viscosity are rather inaccurate in general and we shall therefore omit the values of column 4 of Table V in the computation of the average value of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$: the values quoted in column 5 are then the arithmetic means of columns 2 and 3. The small discrepancies between the

TABLE IV. Values of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA}, Deduced from ε^* and r^* Values from Gaseous Viscosities (argon taken as reference). Experimental sources: see Hirschfelder, Curtiss, and Bird[23]

	ε^*/k, °K	$r^*2^{-\frac{1}{6}}$, A	$\varepsilon^*_{BB}/\varepsilon^*_{AA}$	r^*_{BB}/r^*_{AA}
A	124 116	3.418 3.465	1	1
Kr	190	3.61	1.583	1.049
N_2	91.5 79.8	3.681 3.749	0.713	1.079
O_2	113 88	3.433 3.541	0.838	1.013
CO	110 88	3.590 3.706	0.825	1.060
CH_4	137 144	3.882 3.796	1.171	1.115

TABLE V. Comparison of the Values of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$, Obtained by Various Methods (Tables II, III, and IV). Average Value of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$

	Critical data	Second virial coefficient	Viscosity	Average value
A	1	1	1	1
Kr	1.387	1.361	(1.583)	1.374 ± 0.013
N_2	0.836	0.790	(0.713)	0.813 ± 0.023
O_2	1.022	0.974	(0.838)	0.998 ± 0.024
CO	0.881	0.829	(0.825)	0.855 ± 0.026
CH_4	1.266	1.226	(1.171)	1.246 ± 0.020
				Uncertainty: $\sim \pm 0.02$

values of columns 2 and 3 are due both to experimental errors and to small deviations from the theorem of corresponding states. We believe that the averaging process will in any case reduce these errors and lead to a more reasonable value of $\varepsilon^*_{BB}/\varepsilon^*_{AA}$.

TABLE VI. Comparison of the Values of r^*_{BB}/r^*_{AA}, Obtained by Various Methods (Tables II, III, and IV). Average Value of r^*_{BB}/r^*_{AA}

	Critical data	Second virial coefficient	Viscosity	Average value
A	1	1	1	1
Kr	1.070	1.058	1.049	1.059 ± 0.007
N_2	1.062	1.089	1.079	1.077 ± 0.010
O_2	0.996	1.035	1.013	1.014 ± 0.013
CO	1.070	1.106	1.060	1.079 ± 0.018
CH_4	1.099	1.122	1.115	1.112 ± 0.009
				Uncertainty: $\sim \pm 0.01$

We do exactly the same in Table VI for r^*_{BB}/r^*_{AA} with the difference however that here the values of columns 2, 3, and 4 agree reasonably well with each other and that the average estimates of column 5 are calculated from these three sets of data.

The values of δ and ρ for mixtures of any two substances listed in Tables V and VI are then easily obtained; e.g., for CH_4–Kr, taking CH_4 as reference, we find:

$$\delta = 1.374/1.246 - 1 = \quad 0.104$$

$$\rho = 1.059/1.112 - 1 = -0.048$$

The estimated uncertainties in the average values $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA} of Tables V and VI are respectively ± 0.02 and ± 0.01 (resulting from both experimental errors and deviations from the theorem of corresponding states). This unavoidably leads to rather high inaccuracies in δ and ρ (20% in the case of CH_4–Kr considered above).

Let us now turn to the two other parameters, θ and σ, which

are specific to a given mixture. It has usually been assumed that they could be calculated from the combination rules:

$$\varepsilon^*_{AB} = (\varepsilon^*_{AA}\varepsilon^*_{BB})^{\frac{1}{2}}, \qquad r^*_{AB} = \tfrac{1}{2}(r^*_{AA} + r^*_{BB})$$

which leads to

$$\theta = \sqrt{1 + \delta} - 1 - \tfrac{1}{2}\delta, \qquad \sigma = 0 \tag{63}$$

The theoretical foundations of these rules are, however, rather weak: the first one is supposed to result from a formula derived by London for dispersion forces between unlike molecules, the validity of which is actually restricted to distances much larger than r^*; the second one would only be true for molecules acting as rigid spheres. Many authors tried to check the validity of the combination rules by measuring the second virial coefficients of mixtures. It seems that within the experimental accuracy (unfortunately not very high) both rules are roughly verified.[24]

In view of this situation we shall adopt here the following attitude for comparing the APM with the experimental data:

(a) We shall accept the combination rules (63) as first approximations in order to compute the numerical values of the excess functions, and carry along these lines a detailed comparison of the APM *qualitative* predictions with the experimental data in Section V.

(b) In Section VI, where we discuss the quantitative results of the application of the APM to a series of mixtures, we shall first accept the combination rules (63), and next reject them and look for the best agreement between theory and experiment by considering θ and σ as adjustable parameters.

V. DISCUSSION OF THE QUALITATIVE PREDICTIONS OF THE APM CONCERNING THE MAIN EXCESS FUNCTIONS

Our aim in this section is to investigate the qualitative behavior of the excess functions of the APM and to compare it with the available experimental data. We accept the combination rules (63) as first approximations so that the excess functions are essentially related to the two parameters δ and ρ.

We confine the discussion to the following excess functions:

$$g^E,\ h^E,\ s^E,\ v^E,\ c^E, \quad \text{and} \quad dv^E/dT$$

(where c^E is the excess specific heat at constant pressure.) Their dependency on δ and ρ can be found from:

(a) expressions (36)–(37) and (38)–(39) for the *crude version* and the *refined version* II respectively;

(b) the analytical expressions (45) and (57) for $\omega(\tilde{T})$ and $\eta_0(\tilde{T})$;

(c) the appropriate averages $\langle \varepsilon^* \rangle$ and $\langle r^* \rangle$ (formulas (18)–(19) and (26)–(27)).

Let us once more emphasize that we do not make use here of any expansion of $\langle \varepsilon^* \rangle$ and $\langle r^* \rangle$ in powers of δ and ρ but rather

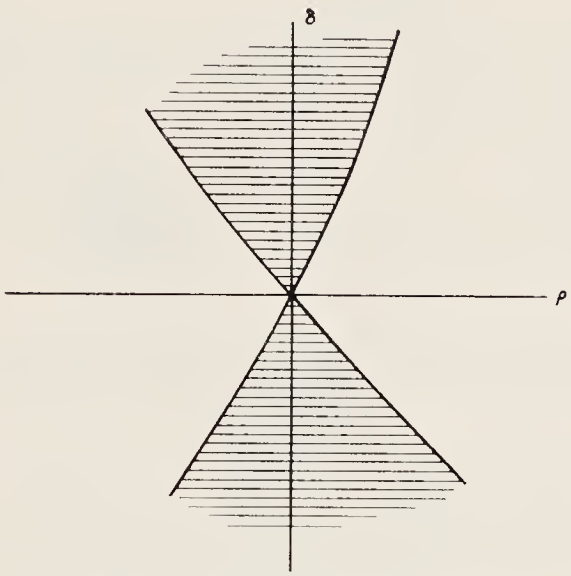

Fig. 3. Schematic representation of the qualitative behavior of s^E, v^E, c^E, and dv^E/dT as functions of ρ and δ ($x_A = x_B = 0.5$). White area = positive sign, shaded area = negative sign.

use their full expressions; for example, we have for the *refined version II*:

$$\langle \varepsilon_A^* \rangle = \varepsilon_{AA}^* \frac{[x_A + x_B(1+\delta)^{\frac{1}{2}}(1+\frac{1}{2}\rho)^6]^2}{[x_A + x_B(1+\delta)^{\frac{1}{2}}(1+\frac{1}{2}\rho)^{12}]} \tag{64a}$$

$$\langle \varepsilon_B^* \rangle = \varepsilon_{AA}^* \frac{[x_A(1+\delta)^{\frac{1}{2}}(1+\frac{1}{2}\rho)^6 + x_B(1+\delta)(1+\rho)^6]^2}{[x_A(1+\delta)^{\frac{1}{2}}(1+\frac{1}{2}\rho)^{12} + x_B(1+\delta)(1+\rho)^{12}]} \tag{64b}$$

and similar expressions for $\langle r_A^* \rangle$ and $\langle r_B^* \rangle$.

We have constructed extensive tables of the above-mentioned excess functions in terms of δ and ρ for $0.6 < \tilde{T}_{AA} < 0.9$ and various mole fractions; it turns out that (a) g^E and h^E are always positive, and (b) s^E, v^E, c^E, and dv^E/dT may be either positive or negative following the relative values of δ and ρ, as schematized in Fig. 3.

These conclusions are valid for both the *crude* and the *refined versions*: the only difference is that the negative domain of the excess functions is somewhat smaller for the crude version, which probably overemphasizes the ρ-effect (size difference of A and B components).

We report in Table VII the signs of the excess functions reported in the literature for eight binary liquid mixtures of simple molecules; the corresponding values of δ and ρ for each mixture are given (first component = reference component A) as well as the temperature and T_{AA}. These values of δ and ρ have been deduced from Tables V and VI, and the reference component has been chosen in such a way that all the δ's are positive.

TABLE VII. Experimental Signs of the Excess Functions of Several Mixtures of Simple Molecules in Relation to the δ and ρ Values

Mixture ($x = 0.5$)	g^E	h^E	s^E	v^E	c^E	$\frac{dv^E}{dT}$	δ	ρ	T, °K	$\tilde{T}_{AA}$	Ref.
CO–CH_4	+	+	−	−			0.457	0.031	91	0.84	9, 25, 26
A–CH_4	+	+	+	+			0.246	0.112	91	0.74	25, 27
CH_4–Kr	+			$\simeq 0$			0.104	−0.048	116	0.74	31
O_2–A	+	+	+	+		+	0.002	−0.014	84	0.68	18, 19, 28, 29
N_2–A	+	+	+	−			0.230	−0.072	84	0.82	18
CO–A				+			0.170	−0.073	84	0.80	18
N_2–O_2	+	+	+	−		−	0.228	−0.058	77	0.75	18, 19, 28, 30
N_2–CO				−			0.052	0.002	84	0.84	18

We notice first that g^E and h^E are positive for all mixtures in agreement with the predictions of the APM. To analyze the behavior of the other excess functions we proceed in the following

manner: in the plane (ρ, δ) we represent each mixture by a circle which is white or black according to the sign of the considered excess function (white = positive, black = negative). The scales of ρ and δ are respectively chosen in such a way that the circles roughly correspond to the uncertainties of Tables V and VI: $\Delta\rho = \pm 0.01$, $\Delta\delta = \pm 0.02$. We also plot on the same graph the boundary between the positive and negative domains predicted

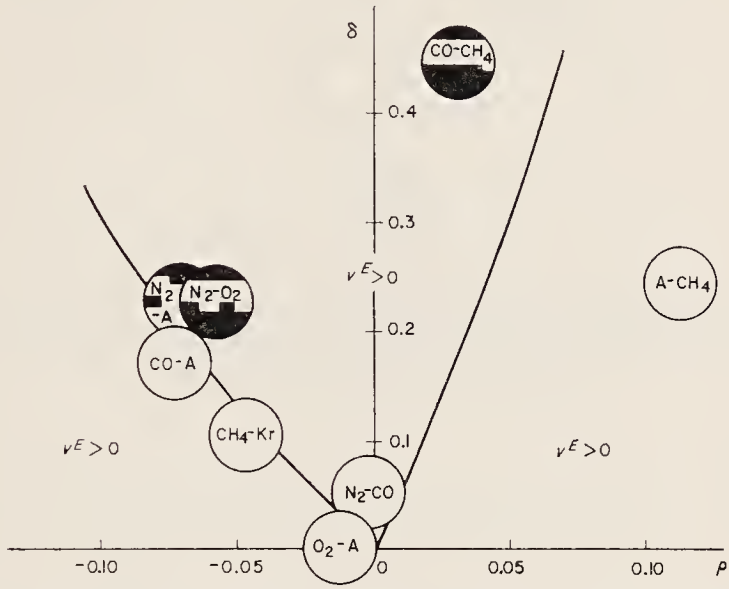

Fig. 4. Qualitative comparison between the experimental excess volumes and the APM predictions. White circles: $v^E > 0$, black circles: $v^E < 0$ $(x = 0.5)$.

by the refined version II (which we believe to be more valuable than the crude model for liquid mixtures). This boundary, which slowly moves with the temperature, is represented here for $\tilde{T}_{AA} = 0.8$, which is roughly the average reduced temperature of the various mixtures of Table VII.

Figures 4, 5, 6, and 7 correspond to v^E, s^E, dv^E/dT, and c^E respectively. Except for c^E, for which no data are presently available, the agreement is quite satisfactory: with the exceptions of a few circles which lie across the boundary, all white and black circles fall in the positive and negative domains respectively.

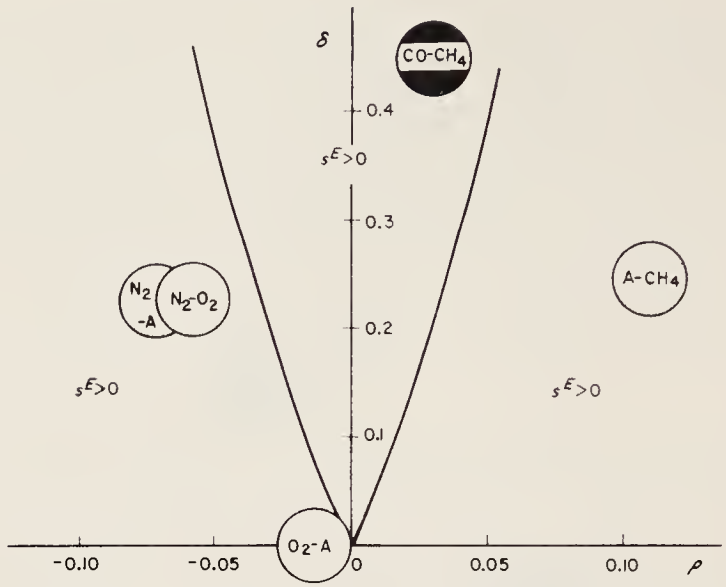

Fig. 5. Qualitative comparison between the experimental excess entropies and the APM predictions. White circles: $s^E > 0$, black circles: $s^E < 0$ ($x = 0.5$).

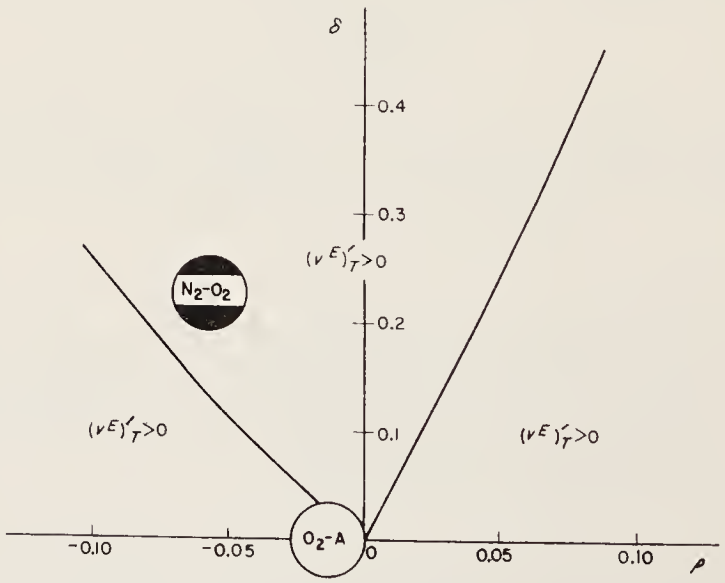

Fig. 6. Qualitative comparison between the experimental $(v^E)'_T = dv^E/dT$ and the APM predictions. White circles: $dv^E/dT > 0$, black circles: $dv^E/dT < 0$ ($x = 0.5$).

In view of the inherent uncertainties in δ and ρ, and of the use of the combination rules, we may conclude that the APM gives

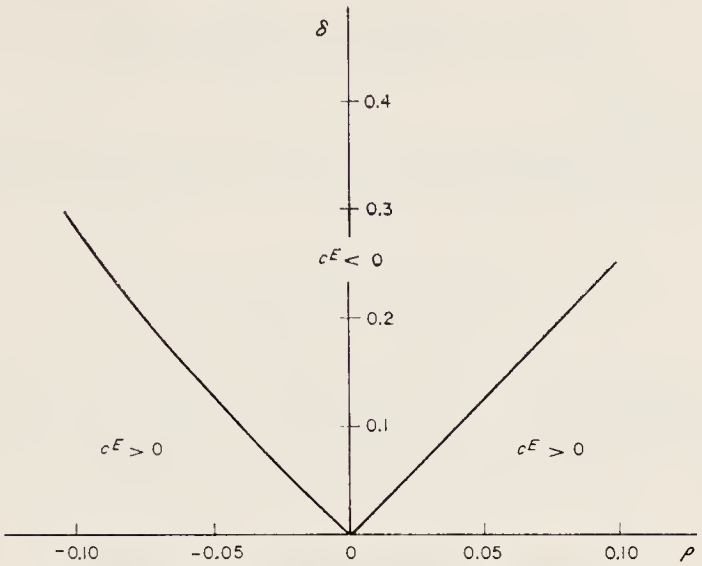

Fig. 7. APM predictions for c^E ($x = 0.5$).

a fair account of the experimental data in as far as the qualitative behavior of the excess functions is considered only.

VI. QUANTITATIVE DISCUSSION OF THE VALIDITY OF THE APM

We shall now compare the quantitative predictions of the APM (*refined version* II) with the excess properties of the following five mixtures:

$$CO\text{–}CH_4,\ A\text{–}CH_4,\ N_2\text{–}O_2,\ N_2\text{–}A, \text{ and } O_2\text{–}A$$

for which all the three most important excess properties, g^E, h^E, and v^E, are accurately known. (We disregard in the discussion the excess entropy s^E because it is not an independent quantity as it is usually obtained from g^E and h^E through the relationship $(h^E - g^E)/T$.)

This section is conveniently divided into two parts. In the first one we review briefly the experimental data for the five

selected mixtures. In the second part we compare the excess functions calculated from the APM with the experimental ones.

A. Review of the Experimental Data

Mixture CO–CH_4

Its excess free energy and volume at 90.7°K have been measured by Mathot, Staveley, *et al.*:[9]

$$g^E = x(1 - x)\{111.9 - 4.0(2x - 1)\} \text{ cal/mole} \tag{65}$$

$$v^E = x(1 - x)\{-1.30 + 0.41(2x - 1)\} \text{ cm}^3\text{/mole} \tag{66}$$

where x is the mole fraction of CH_4. The excess enthalpy and volume at 91.2°K were determined by Lambert and Simon:[25]

$$h^E = x(1 - x)\{101.5 + 7.0(2x - 1)\} \text{ cal/mole} \tag{67}$$

$$v^E = x(1 - x)\{-1.36 + 0.29(2x - 1)\} \text{ cm}^3\text{/mole} \tag{68}$$

The two sets of measurements of v^E agree reasonably well with each other (cf. Fig. 3 of Ref. 25). The excess enthalpy has also been measured by Pool and Staveley[26] by a calorimetric technique which seems somewhat less advanced than the one used by Lambert and Simon. Their results are in moderate agreement with (67).

From the above data we assign the following values to g^E, h^E, and v^E at 91°K:

$$g^E/kT = x(1 - x)\{0.619 - 0.022(2x - 1)\} \tag{69}$$

$$h^E/kT = x(1 - x)\{0.561 + 0.039(2x - 1)\} \tag{70}$$

$$v^E = x(1 - x)\{-1.33 + 0.35(2x - 1)\} \text{ cm}^3\text{/mole} \tag{71}$$

with an accuracy of ~2% in g^E and h^E and ~4% in v^E.

Mixture A–CH_4

Its excess free energy has been measured by Mathot and Lefebvre[27] at 86.7°K:

$$g^E/kT = x(1 - x)\{0.422 - 0.038(2x - 1)\} \tag{72}$$

where x is the mole fraction of CH_4. The excess enthalpy and volume were determined by Lambert and Simon[25] at 91.2°K:

$$h^E = x(1 - x)\{98.4 - 4.8(2x - 1)\} \text{ cal/mole} \quad (73)$$

$$v^E = x(1 - x)\{0.72 - 0.17(2x - 1)\} \text{ cm}^3\text{/mole} \quad (74)$$

A few measurements of v^E by Mathot and Lefebvre[27] confirm (74).

From the above data we assign the following values to g^E, h^E, and v^E at 91°K:

$$g^E/kT = x(1 - x)\{0.395 - 0.037(2x - 1)\} \quad (75)$$

$$h^E/kT = x(1 - x)\{0.546 - 0.027(2x - 1)\} \quad (76)$$

$$v^E = x(1 - x)\{0.72 - 0.17(2x - 1)\} \text{ cm}^3\text{/mole} \quad (77)$$

with the respective accuracies of ~2% in g^E and h^E, and ~4% in v^E.

Mixture N_2–O_2

Pool, Staveley, *et al.*[18] reported the following values for g^E and v^E at 84°K:

$$g^E = x(1 - x)\{36.81 + 1.67(2x - 1) - 0.33(2x - 1)^2\} \text{ cal/mole} \quad (78)$$

$$v^E = x(1 - x)\{-1.2574 + 0.073(2x - 1)\} \text{ cm}^3\text{/mole} \quad (79)$$

where x is the mole fraction of O_2. The excess enthalpy has been measured at 77°K by Knobler *et al.*:[19] their measurements can roughly be fitted by the following formula:

$$h^E = x(1 - x)\{42 + 10(2x - 1) + 20(2x - 1)^2\} \text{ cal/mole} \quad (80)$$

The excess volume at 77°K was reported by Knaap *et al.*[28] and can be represented roughly as:

$$v^E = x(1 - x)\{-0.84 + 0.44(2x - 1)\} \text{ cm}^3\text{/mole} \quad (81)$$

(this expression differs considerably from (79) but one should not forget that the corresponding temperatures are 7° apart). Finally Knobler *et al.*[19] calculated the excess free energy at 77°K from the

vapor pressure data of Armstrong, Goldstein, and Roberts,[30] which can be fitted by:

$$g^E = x(1 - x)\{40 + 4(2x - 1) + 4(2x - 1)^2\} \text{ cal/mole} \quad (82)$$

in rough agreement with (78).

We shall adopt the last three values for h^E, v^E, and g^E at 77°K, i.e.,

$$g^E/kT = x(1 - x)\{0.262 + 0.026(2x - 1) + 0.026(2x - 1)^2\} \quad (83)$$

$$h^E/kT = x(1 - x)\{0.275 + 0.065(2x - 1) + 0.130(2x - 1)^2\} \quad (84)$$

$$v^E = x(1 - x)\{-0.84 + 0.44(2x - 1)\} \text{ cm}^3\text{/mole} \quad (85)$$

Their relative accuracies lie probably around 5%.

Mixture N_2–A

Accurate values of g^E, h^E, and v^E at 84°K have been reported by Pool, Staveley, *et al.*:[18]

$$g^E/kT = x(1 - x)\{0.1970 + 0.0099(2x - 1) - 0.0020(2x - 1)^2\} \quad (86)$$

$$h^E/kT = x(1 - x)\{0.2897 - 0.0774(2x - 1)\} \quad (87)$$

$$v^E = x(1 - x)\{-0.7191 + 0.0025(2x - 1)\} \text{ cm}^3\text{/mole} \quad (88)$$

where x is the mole fraction of A. The accuracy in all three cases is of the order of 2%.

Mixture O_2–A

Pool, Staveley, *et al.*[18] have reported values of g^E, h^E, and v^E at 84°K:

$$g^E/kT = x(1 - x)\{0.2126 + 0.0010(2x - 1) + 0.0017(2x - 1)^2\} \quad (89)$$

$$h^E/kT = x(1 - x)\{0.3430 + 0.0450(2x - 1)\} \quad (90)$$

$$v^E = x(1 - x)\{0.5442 - 0.0011(2x - 1)\} \text{ cm}^3\text{/mole} \quad (91)$$

with an accuracy of about 2% (where x is the mole fraction of A). These results agree reasonably well with measurements of other authors (Narinskii[29] for g^E, Knobler *et al.*[19] for h^E and Knaap *et al.*[28] for v^E).

B. Comparison of the Experimental and Theoretical Values of g^E, h^E, and v^E

We shall proceed as follows:

(a) The theoretical values of the excess functions are calculated from Eqs. (38), (39), and (41). The values of δ and ρ for the various mixtures are quoted in Table VII (first component = reference component). The required values of ε^*/k and r^{*3} for the first component are given in Table I with the exception of O_2, for which the values are: $\varepsilon^*/k = 123.0°K$, $r^{*3} = 56.1$ A^3, $N_a r^{*3} = 33.8$ cm^3/mole^{-1} (obtained from the ε^* and r^* values of A and from the $\varepsilon^*_{BB}/\varepsilon^*_{AA}$ and r^*_{BB}/r^*_{AA} values of O_2 from Tables V and VI).

(b) We first calculate a set of values of g^E, h^E, and v^E under the assumption that the combination rules (6) and (7) are valid.

(c) We next consider ε^*_{AB} and r^*_{AB} (or equivalently θ and σ) as two adjustable parameters and we look for the best agreement between the theoretical and experimental curves of g^E, h^E, and v^E simultaneously; this will show us how far a quantitative agreement may be reached with the APM by altering the commonly accepted combination rules. This adjustment of θ and σ was achieved by the method of least squares on an electronic computer in the following manner: for each excess function $X^E (= g^E, h^E,$ or $v^E)$ we compute the (dimensionless) sum:

$$S(X^E) = \sum_x \left(\frac{X^E_{\text{th.}}(x) - X^E_{\text{exp.}}(x)}{X^E_{\text{exp.}}(x)} \right)^2 \tag{92}$$

with $x = 0.2$, 0.4, 0.5, 0.6, and 0.8, for arbitrary values of θ and σ, and we look for those particular values which give to the sum

$$S(g^E) + S(h^E) + S(v^E) \tag{93}$$

its minimum value.

When comparing the predictions of the APM with the experimental data one should always keep in mind that δ and ρ are subject to errors amounting to ± 0.02 and ± 0.01 respectively; this fact may introduce quite large uncertainties in the calculated excess functions. For example, assuming the validity of the combinations rules, one has the approximate form for g^E:[32]

$$g^E \simeq x_A x_B (A\delta^2 + B\rho^2)$$

where A, B are constants. Then for relatively small values of δ and ρ, e.g., $\delta = 0.10$, $\rho = 0.04$, one has

$$g^E \simeq x_A x_B\{0.0100A + 0.0016B\}$$

with the lower and upper limits:

$$g^E \simeq x_A x_B\{0.0064A + 0.0009B\}$$

$$g^E \simeq x_A x_B\{0.0144A + 0.0025B\}$$

In such a case the uncertainty in g^E is of the order of 50%.

With this in mind, one should consider the adjusted values of θ and σ with great caution: their eventual deviations from the combination rules may be physically meaningful but it may also happen that such deviations actually result accidentally from our inaccurate knowledge of δ and ρ (especially when these two parameters have small values).

We now discuss successively the five liquid mixtures selected in part A of the present section. The results are shown in diagrams consisting of three parts: the central one contains the experimental curves of g^E/kT $(\equiv G^E)$, $h^E/kT(\equiv H^E)$, and v^E as functions of the mole fractions; the left- and right-hand parts show the corresponding theoretical curves for the combination rules and for the adjusted values of θ and σ respectively.

Mixture CO–CH_4 (see Fig. 8)

$$T = 91°K, \qquad \tilde{T}_{AA} = 0.838$$
$$\delta = 0.45_7, \qquad \rho = 0.03_1$$

(a) Combination rules

$$\theta = -0.021_8, \qquad \sigma = 0 \tag{94}$$

The calculated curves for g^E, h^E, and v^E are in very reasonable agreement with the experimental ones.

(b) Adjustment of θ and σ

$$\theta = -0.027_9, \qquad \sigma = 0.002_0 \tag{95}$$

This rather slight modification in θ and σ brings the calculated excess functions into almost perfect agreement with the experimental data.

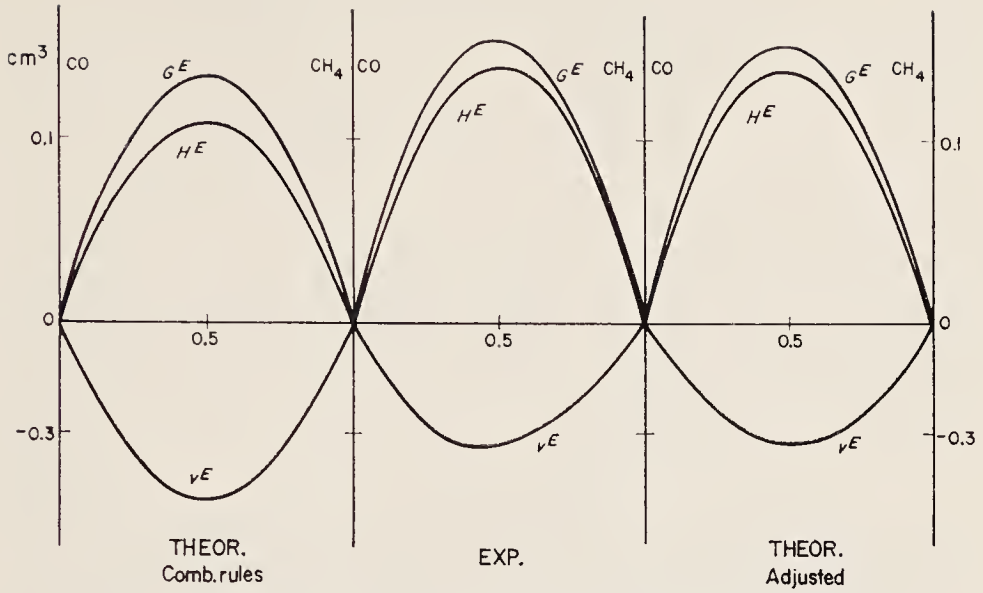

Fig. 8. Experimental and theoretical excess functions g^E/kT, h^E/kT, and v^E of the system CO–CH_4 at 91°K.

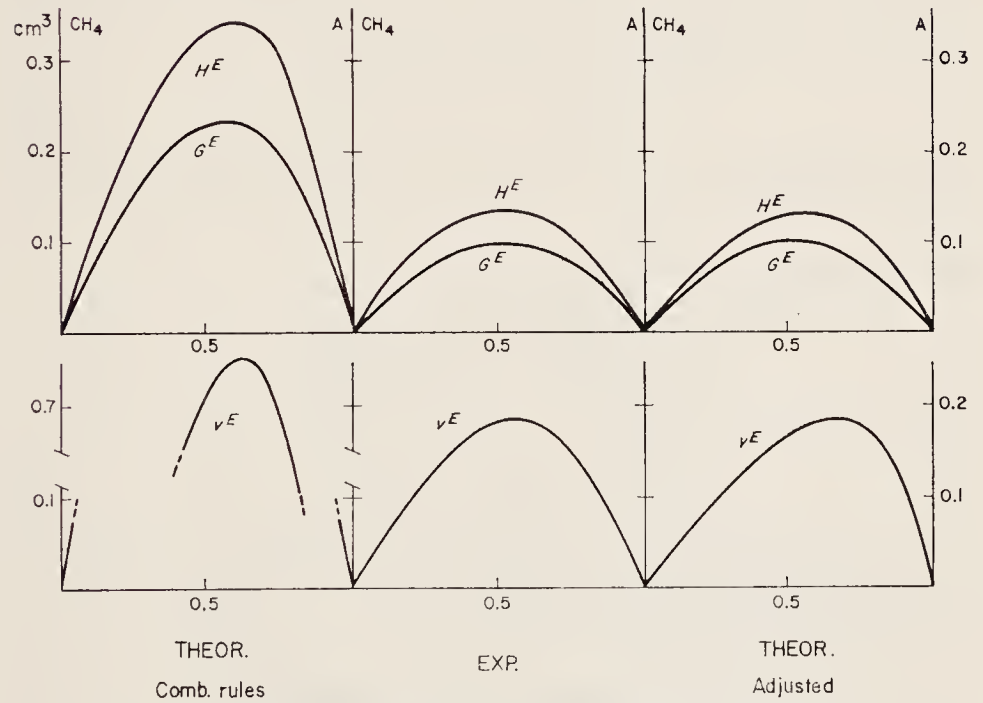

Fig. 9. Experimental and theoretical excess functions g^E/kT, h^E/kT, and v^E of the system A–CH_4 at 91°K.

Mixture A–CH_4 (see Fig. 9)

$$T = 91°K, \qquad \tilde{T}_{AA} = 0.739$$
$$\delta = 0.24_6, \qquad \rho = 0.11_2$$

(a) Combination rules

$$\theta = -0.006_8, \qquad \sigma = 0 \tag{96}$$

The theoretical curves are systematically too high by factors of 2 to 4.

(b) Adjustment of θ and σ

$$\theta = +0.031_1, \qquad \sigma = -0.007_8 \tag{97}$$

A good agreement is reached (except for a strong skewness in v^E), but at the price of big changes in the values of θ and σ.

Actually we are dealing here with a system where the difference in size of the two components is appreciable ($\rho > 0.1$) and this might well go beyond the limit of validity of the APM. It is, however, interesting to note that an evaluation of ε^*_{AB} and r^*_{AB} for the present system has been made by Thomaes *et al.*[33] from second virial coefficients. This leads roughly to:

$$\theta \simeq 0.004, \qquad \sigma = -0.004 \tag{98}$$

i.e., to deviations from the combination rules in the same direction as in Eq. (97).

Mixture N_2–O_2 (see Fig. 10)

$$T = 77°K, \qquad \tilde{T}_{AA} = 0.748$$
$$\delta = 0.22_8, \qquad \rho = -0.05_8$$

(a) Combination rules

$$\theta = -0.005_8, \qquad \sigma = 0 \tag{99}$$

The theoretical curves for g^E and h^E are too high by a factor of 2 while v^E is too small by a factor of 2.

(b) Adjustment of θ and σ

$$\theta = 0.003_7, \qquad \sigma = -0.000_7 \tag{100}$$

This leads to a substantial agreement for g^E, h^E, and v^E.

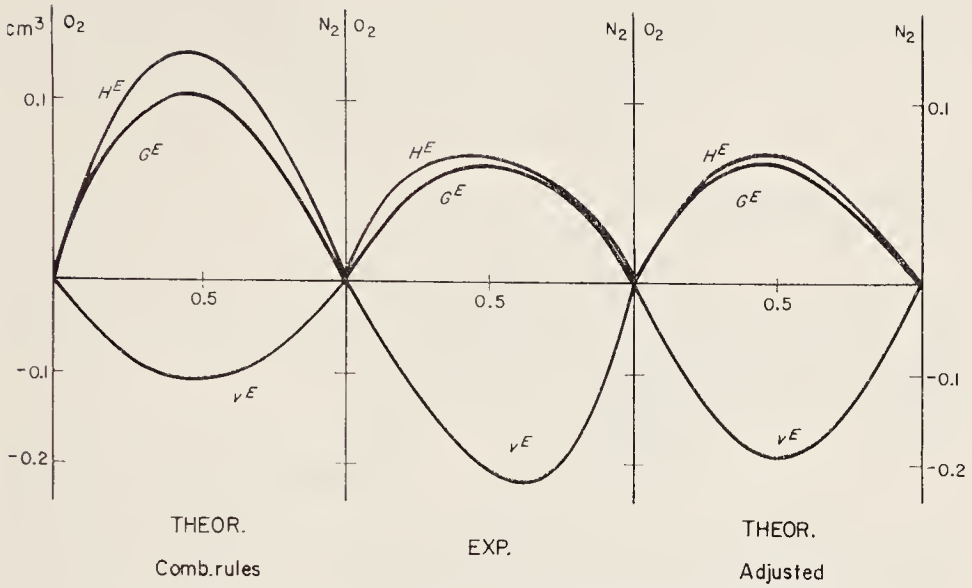

Fig. 10. Experimental and theoretical excess functions g^E/kT, h^E/kT, and v^E of the system N_2–O_2 at 77°K.

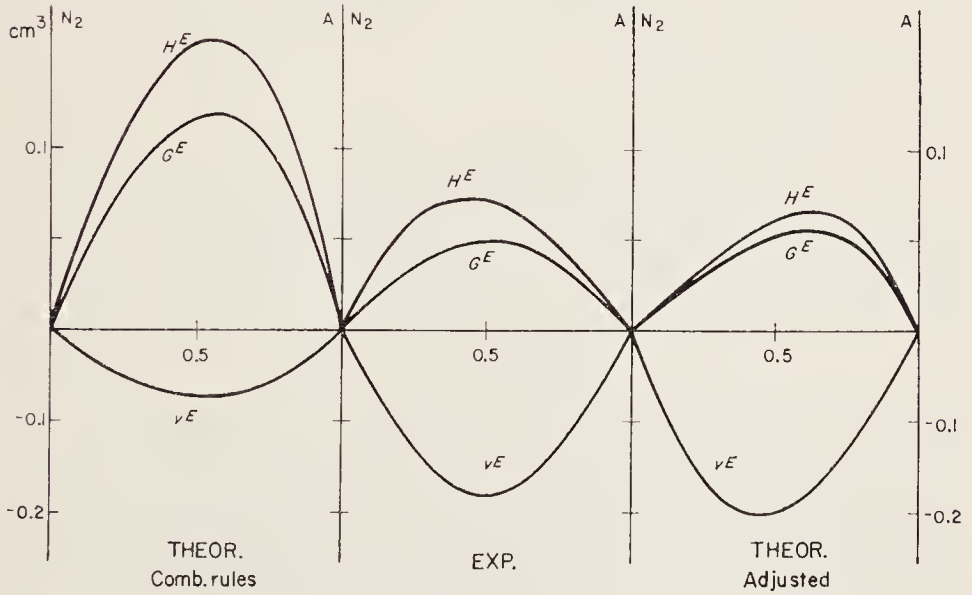

Fig. 11. Experimental and theoretical excess functions g^E/kT, h^E/kT, and v^E of the system N_2–A at 84°K.

Mixture N_2–A (see Fig. 11)

$$T = 84°K, \qquad \tilde{T}_{AA} = 0.816$$
$$\delta = 0.23_0, \qquad \rho = -0.07_2$$

(a) Combination rules

$$\theta = -0.005_9, \qquad \sigma = 0 \tag{101}$$

The calculated values of g^E and h^E are exaggerated by a factor ~ 2.5; v^E is too small by a factor of 3.
(b) Adjustment of θ and σ

$$\theta = 0.013_5, \qquad \sigma = 0.000_3 \tag{102}$$

The calculated values of g^E, h^E, and v^E are roughly in agreement with experimental data, except for skewness.

Mixture O_2–A (see Fig. 12)

$$T = 84°K, \qquad \tilde{T}_{AA} = 0.683$$
$$\delta = 0.00_2, \qquad \rho = -0.01_4$$

(a) Combination rules

$$\theta = 0.000_0, \qquad \sigma = 0 \tag{103}$$

All the theoretical excess functions are practically equal to zero, in marked disagreement with the experimental data.
(b) Adjustment of θ and σ

$$\theta = -0.012_6, \qquad \sigma = 0.001_7 \tag{104}$$

The agreement is almost perfect for all three excess functions.

The present analysis indicates a very rough agreement of the APM with the experimental data when the combination rules (6.3) are assumed to be valid. On the other hand, the adjustment of the two parameters θ and σ leads to a good agreement in general for the three excess functions g^E, h^E, and v^E. This is, of course, an argument in favour of the APM though probably not a very

strong one: we have already pointed out (in the beginning of this section) how careful one has to be in the interpretation of the adjusted values of θ and σ. It seems that the $|\sigma|$ values are always

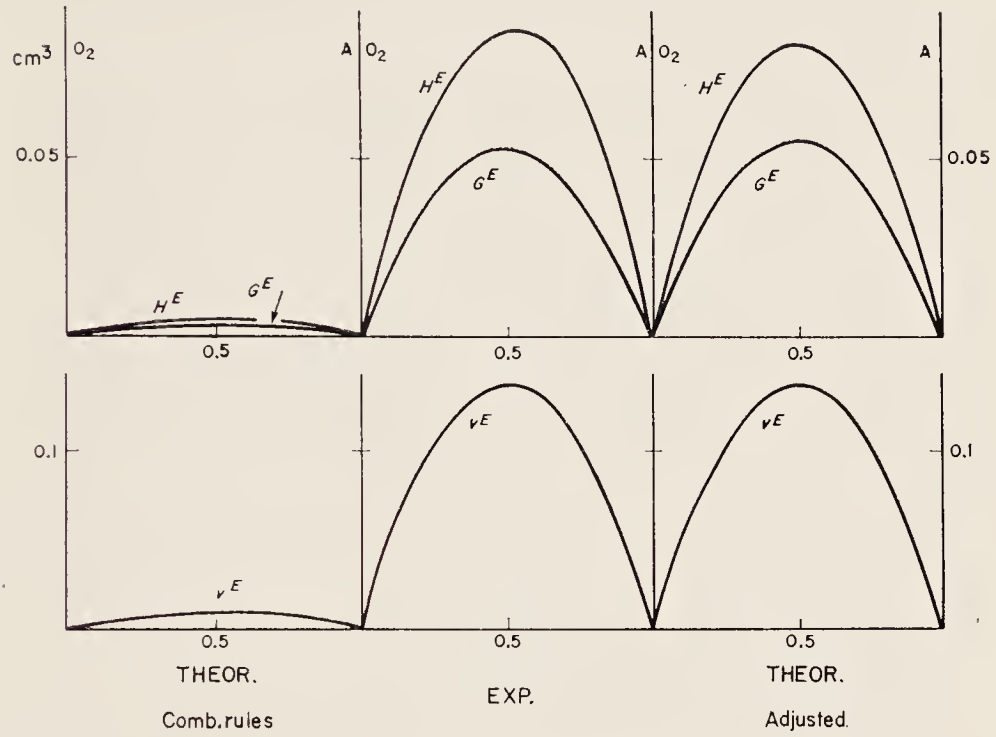

Fig. 12. Experimental and theoretical excess functions g^E/kT, h^E/kT, and v^E of the system O_2–A at 84°K.

small (less than 0.002 except for the system A–CH_4 where ρ is unusually large); the approximation

$$\sigma \simeq 0$$

(i.e., the combination rule (7)) seems therefore very reasonable. No general trend seems to appear in the adjusted values of θ.

VII. FINAL COMMENTS AND CONCLUSIONS

From the qualitative discussion of Section V, we have seen that the APM is a valuable tool for predicting the sign of the main

excess functions of mixtures of roughly spherical molecules. The situation is less favorable from the quantitative point of view: we have just seen in Section VI that in general g^E, h^E, and v^E appear to be wrong by a factor of the order of 2 in one or other direction (under the assumption however that the combination rules are valid).

A part of these discrepancies is undoubtedly due to the uncertainty in the δ and ρ values and some inadequacy of the combination rules (especially (6)), and is clearly irrelevant to the soundness of the APM itself. The remaining part of the observed discrepancies arises from oversimplifications in the underlying assumptions of the model. We here limit the discussion to two of them:

(1) The average interactions $\langle \varepsilon_A(r) \rangle$ and $\langle \varepsilon_B(r) \rangle$ are evaluated under the assumption of a random distribution of the A and B molecules in space (*random mixing*). This point has been discussed by Rice[13] using the quasi-chemical approximation: the corrections to the various excess functions appear to be of the order of 5–10%.

(2) The three pair potentials $\varepsilon_{AA}(r)$, $\varepsilon_{AB}(r)$, and $\varepsilon_{BB}(r)$ are submitted to the following increasing restrictions in the development of the APM (cf. Section II):

(a) they must conform to Eq. (9);

(b) they must be of the Lennard-Jones (n–m) type;

(c) for practical calculations one takes $n = 6$, $m = 12$. It is not easy to estimate the influence of deviations from (a) and (b) upon the excess functions. On the contrary, the replacement of a 6–12 potential by an arbitrary n–m potential is easily worked out: Table VIII shows the values of g^E, h^E, and v^E for different values of δ and ρ, and for several choices of n–m. In the worst case ($\delta = 0.00$, $\rho = 0.05$) the excess functions vary by $\sim 50\%$ when going from a 6–12 to a 7–14 potential. Note however that the dependence of the excess functions on n–m comes in through the parameter ρ only[37] and that this effect therefore remains relatively small when δ is large.

To conclude, we believe that the present analysis of the APM shows the limitations of the model itself and of its practical application; in view of these limitations it would be hardly reasonable to expect a much better quantitative agreement than the one obtained in Section VI.

TABLE VIII. Theoretical Values of g^E, h^E, and v^E for the APM (Refined Version II) at a Mole Fraction of 0.5, for Various Potentials n–m, Assuming the Validity of the Combination Rules ($v^* = N_a r^{*3}/\sqrt{2}$)

(a) $\delta = 0.00$, $|\rho| = 0.05$

n \ m	12	14
6	$g^E/kT = 0.039$	0.046
	$h^E/kT = 0.063$	0.074
	$v^E/v^* = 0.0059$	0.0069
7	$g^E/kT = 0.046$	0.054
	$h^E/kT = 0.074$	0.086
	$v^E/v^* = 0.0066$	0.0077

(b) $\delta = 0.30$, $\rho = 0.05$

n \ m	12	14
6	$g^E/kT = 0.111$	0.119
	$h^E/kT = 0.123$	0.135
	$v^E/v^* = 0.0011$	0.0019
7	$g^E/kT = 0.119$	0.128
	$h^E/kT = 0.135$	0.148
	$v^E/v^* = 0.0016$	0.0025

(c) $\delta = 0.30$, $\rho = -0.05$

n \ m	12	14
6	$g^E/kT = 0.122$	0.131
	$h^E/kT = 0.132$	0.146
	$v^E/v^* = -0.0079$	−0.0071
7	$g^E/kT = 0.131$	0.142
	$h^E/kT = 0.146$	0.161
	$v^E/v^* = -0.0074$	−0.0065

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PART II

NON-EQUILIBRIUM STATISTICAL MECHANICS

MICROSCOPIC APPROACH TO EQUILIBRIUM AND NON-EQUILIBRIUM PROPERTIES OF ELECTROLYTES

P. RÉSIBOIS and N. HASSELLE-SCHUERMANS, *Université Libre de Bruxelles, Brussels, Belgium*

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I. INTRODUCTION

Since the early days of Faraday and Arrhénius, electrolytic solutions have provided a most challenging field for both the experimental and the theoretical physico-chemist. In particular, the long range of the Coulomb forces between the electric charges located on the ions gives rise to highly non-trivial effects on the equilibrium and transport properties of electrolytes.

The first satisfactory explanation of these effects was given, in the twenties, by Debye, Hückel, Onsager, and Falkenhagen (see, for instance, Ref. 8). Using a remarkably clever combination of microscopic and macroscopic concepts, they were able to describe the behavior of dilute electrolytes by the famous "limiting laws".

For equilibrium theory, one had to wait until the basic work of Mayer[22] before getting a rigorous derivation of the Debye–Hückel limiting law, on the basis of statistical mechanics. For transport phenomena, the situation was even worse: as long as no general method existed for treating irreversible phenomena in a rigorous fashion, it was impossible to obtain a proper treatment of electrolytic conductance.

However, the recent developments in non-equilibrium statistical mechanics, and the success of its application in another field of physics where the long-range Coulomb forces play a major role, namely plasma physics, have led various authors to investigate the limiting laws for transport phenomena in electrolytes from a

microscopic point of view.[5,9,12,13] Needless to say, this question is much more difficult than the corresponding equilibrium problem and very drastic simplifications have to be used in the description of the interactions between the solvent molecules and the ions. Nevertheless, it is now possible to formulate this problem in a mathematically consistent fashion and with the same degree of rigor as the Mayer's equilibrium theory; in particular, one may derive sufficient conditions for the validity of the conductance limiting law.

The aim of the present paper is to give a general report of the work realized in that field, at Brussels University. We shall show how the theory of irreversible processes due to Prigogine and his co-workers allows both equilibrium and non-equilibrium properties of electrolytes to be formulated in a unified manner and how, in simple cases at least, the known results of the limiting laws may be rigorously justified on a statistical basis. In order to make this article a reasonable length, detailed mathematical proofs will often be replaced by arguments which are "physically obvious". The reader interested in the mathematical details will often be referred to the original papers as well as to existing monographs.[1,27,31]

No attempt will be made here to extend our results beyond the simple lowest-order limiting laws; the often "ad hoc" modifications of these laws to higher concentrations are discussed in many excellent books,[8,11,14] but we shall not try to justify them here. As a matter of fact, for equilibrium as well as for non-equilibrium properties, the rigorous extension of the microscopic calculation beyond the first term seems outside the present power of statistical mechanics, because of the rather formidable mathematical difficulties which arise. The main interests of a microscopic theory lie both in the justification of the assumptions which are involved in the phenomenological approach and in the possibility of extending the mathematical techniques to other problems where a microscopic approach seems necessary: in the particular case of the limiting laws, obvious extensions are in the direction of other transport coefficients of electrolytes (viscosity, thermal conductivity, questions involving polyelectrolytes) and of plasma physics, as well as of quantum phenomena where similar effects may be expected (conductivity of metals and semi-

conductors). Although calculations in these various directions are now developing, we shall not consider these questions here.

Section II deals with the general formalism of Prigogine and his co-workers. Starting from the Liouville equation, we derive an exact transport equation for the one-particle distribution function of an arbitrary fluid subject to a weak external field. This equation is valid in the so-called "thermodynamic limit", i.e. when the number of particles $N \to \infty$, the volume of the system $\Omega \to \infty$, with $N/\Omega = C$ finite. As a by-product, we obtain very easily a formulation for the equilibrium pair distribution function of the fluid as well as a general expression for the conductivity tensor.

In Section III, we discuss the equilibrium properties of dilute strong electrolytes; we first give a brief critical summary of the macroscopic approach and we consider next the microscopic theory, following the work of Balescu,[1] and we try to make as clear as possible the approximations involved.

The next section is devoted to the analysis of the simplest transport property of ions in solution: the conductivity in the limit of infinite dilution. Of course, in non-equilibrium situations, the solvent plays a very crucial role because it is largely responsible for the dissipation taking part in the system; for this reason, we need a model which allows the interactions between the ions and the solvent to be discussed. This is a difficult problem which cannot be solved in full generality at the present time. However, if we make the assumption that the ions may be considered as heavy with respect to the solvent molecules, we are confronted with a "Brownian motion" problem; in this case, the theory may be developed completely, both from a macroscopic and from a microscopic point of view.

As soon as the concentration of the solute becomes finite, the coulombic forces between the ions begin to play a role and we obtain both the well-known relaxation effect and an electrophoretic effect in the expression for the conductivity. In Section V, we first briefly recall the semi-phenomenological theory of Debye–Onsager–Falkenhagen, and we then show how a combination of the ideas developed in the previous sections, namely the treatment of long-range forces as given in Section III and the Brownian model of Section IV, allows us to study various microscopic

models for the relaxation effect. The connection with the above-mentioned microscopic approaches is also discussed.

It is well-known that the electrophoretic effect involves the hydrodynamical properties of the solvent in a very crucial way; for this reason, the theory of this effect is rather difficult. However, using a Brownian approximation for the ions, we have been able to obtain recently a microscopic description of this effect. This problem, together with the more general question of long-range hydrodynamical correlations, is discussed in Section VI.

Finally, five appendices contain some mathematical problems which were not considered in the main text.

Most of the work reported in this paper has been realized in the department of Professor I. Prigogine, at Brussels University. We wish to thank him for his continuous encouragement during its realization as well as for his helpful suggestions and criticisms. Many thanks are also due to Professors R. Balescu, H. T. Davis (Minnesota University), and J. Lebowitz (Yeshiva University, New York), who, in one way or another, took an essential part in the elaboration of the results presented here.

II. THE GENERALIZED TRANSPORT EQUATION

A. The Liouville Equation and Its Formal Solution

We consider a system of N particles, enclosed in a box of volume Ω and submitted to an external electric field $\mathbf{E}(t)$.

The Hamiltonian is written:

$$H' = H + H^E \tag{1}$$

where the "internal" Hamiltonian:

$$H = H_0 + \lambda V = \sum_{j=1}^{N} \frac{p_j^2}{2m_j} + \lambda \sum_{i>j} V^{ij}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{2}$$

corresponds to both the kinetic energy, H_0, and the interaction energy V between the particles; this latter is scaled with the dimensionless parameter λ.

The "external" part

$$H^E = -\sum_{j=1}^{N} Z_j e \mathbf{E}(t) \mathbf{r}_j \tag{3}$$

describes the interactions with the external field, $Z_j e$ denoting the charge of particle j.

In principle, with given initial conditions, the time evolution of the coordinates and momenta $(\mathbf{r}_j, \mathbf{p}_j)$ of each particle is given by Hamilton's equations:[15]

$$\dot{\mathbf{r}}_j = \frac{\partial H'}{\partial \mathbf{p}_j}; \qquad \dot{\mathbf{p}}_j = -\frac{\partial H'}{\partial \mathbf{r}_j} \tag{4}$$

However, in problems involving a large number of particles, it is usually assumed that the system may be described at the initial time by an *N-particle distribution function*[40]

$$\rho_N(\mathbf{r}_1 \ldots \mathbf{r}_N;\ \mathbf{p}_1 \ldots \mathbf{p}_N;\ 0) \tag{5}$$

which gives the probability of finding the system at time $t = 0$ with coordinates between $\mathbf{r}_1$ and $\mathbf{r}_1 + d\mathbf{r}_1 \ldots \mathbf{p}_N$ and $\mathbf{p}_N + d\mathbf{p}_N$. It is normalized to one

$$\int \rho_N(\mathbf{r}_1 \ldots \mathbf{r}_N;\ \mathbf{p}_1 \ldots \mathbf{p}_N;\ 0)\, d\mathbf{r}_1 \ldots d\mathbf{p}_N = 1 \tag{6}$$

Taking into account that the particles of the system all move according to Hamilton's equations (4), it is easily shown that the distribution function at later times, $t > 0$, is determined by the *Liouville equation*[27,40]

$$\partial_t \rho_N(\mathbf{r}_1 \ldots \mathbf{p}_N;\ t) = \{H', \rho_N(\mathbf{r}_1 \ldots \mathbf{p}_N;\ t)\} \tag{7}$$

where the so-called Poisson's bracket is defined by:

$$\{H', \rho_N\} = \sum_{i=1}^{N} \left(\frac{\partial H'}{\partial \mathbf{r}_i} \frac{\partial \rho_N}{\partial \mathbf{p}_i} - \frac{\partial H'}{\partial \mathbf{p}_i} \frac{\partial \rho_N}{\partial \mathbf{r}_i} \right) \tag{8}$$

Let us now introduce some convenient notation. We shall often write:

$$\begin{aligned} r &\equiv \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\} \equiv \{\mathbf{r}\} \\ p &\equiv \{\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N\} \equiv \{\mathbf{p}\} \end{aligned} \tag{9}$$

when no ambiguity is possible.

Also, we shall write the Liouville equation (7) as

$$i\partial_t \rho_N = L' \rho_N \tag{10}$$

where we have introduced the Hermitian *Liouville operator*:

$$L'\rho_N = i\{H', \rho_N\} \tag{11}$$

In correspondence with the decompositions (1) and (2), we may write:

$$L' = L + L^E \tag{12}$$

$$L = L_0 + \lambda\delta L \tag{13}$$

$$L_0 = -i\sum_j \mathbf{v}_j \frac{\partial}{\partial \mathbf{r}_j} \equiv -iv\frac{\partial}{\partial r} \tag{14}$$

$$\delta L = i\sum_j \frac{\partial V}{\partial \mathbf{r}_j}\frac{\partial}{\partial \mathbf{p}_j} \equiv i\frac{\partial V}{\partial r}\frac{\partial}{\partial p} \tag{15}$$

$$L^E = -i\sum_j Z_j e\mathbf{E}(t)\frac{\partial}{\partial \mathbf{p}_j} \equiv -iZeE(t)\frac{\partial}{\partial p} \tag{16}$$

The formal similarity between Eq. (10) and the time-dependent Schrödinger equation is striking, and we shall indeed develop methods which are very reminiscent of quantum mechanics. In particular, we may calculate the eigenfunctions and eigenvalues of the unperturbed Liouville operator L_0. We look for solutions of:

$$L_0\phi_k(r) = \Lambda_k^0\phi_k(r) \tag{17}$$

subject to periodic boundary conditions.

It can be immediately shown that:

$$\phi_k(r) = \Omega^{-N/2}e^{ikr} \tag{18}$$

$$\Lambda_k^0 = kv \tag{19}$$

with

$$k = 2\pi n/\Omega^{1/3}\ (n = 0, 1, \ldots) \tag{20}$$

In accordance with Eq. (9), we have introduced the notation:

$$\begin{aligned} k &\equiv \{\mathbf{k}_1, \ldots, \mathbf{k}_N\} \equiv \{\mathbf{k}\} \\ n &\equiv \{\mathbf{n}_1 \ldots \mathbf{n}_N\} \equiv \{\mathbf{n}\} \end{aligned} \tag{21}$$

The eigenfunctions $\phi_k(r)$ are normalized to one:

$$\int \phi_k^*(r)\phi_{k'}(r)dr = \delta_{kk'}^{kr} \begin{cases} = 1 & k = k' \\ = 0 & k \neq k' \end{cases} \tag{22}$$

and as in quantum mechanics they are interpreted as the representation in configurational space of the corresponding proper vectors $|k\rangle$ in Hilbert space. Using Dirac's[7] notation, we write:

$$\phi_k(r) = \langle r|k\rangle \tag{23}$$

$$\langle k|k'\rangle = \delta_{kk'}^{kr} \text{ (orthogonality)} \tag{24}$$

$$\sum_k |k\rangle\langle k| = I \text{ (completeness)} \tag{25}$$

where I is the unit operator.

After these technical preliminaries, we may consider the solution of the Liouville equation (10). However, we shall not discuss the most general situation but we shall limit ourselves to the special case where:

(1) the initial condition $\rho_N(r\,;p\,;0)$ is independent of the external field,

(2) this field, $\mathbf{E}(t)$, is sufficiently weak for us to treat it by a *first*-order perturbation calculus.

In this way, we shall be able to calculate the linear response of the system. For such a linear problem, we may as well consider an oscillating field with frequency ω:

$$\mathbf{E}(t) = \mathbf{E}e^{-i\omega t} \tag{26}$$

More general cases would be obtained by a superposition of elementary fields of the type (26) with various frequencies.

If we expand the distribution function as a power series in the field:

$$\rho_N(t) = \rho_N^{(0)}(t) + \rho_N^{(1)}(t) + \ldots \tag{27}$$

we obtain from Eqs. (10) and (12):

$$i\partial_t \rho_N^{(0)}(t) = L\rho_N^{(0)}(t) \tag{28}$$

$$i\partial_t \rho_N^{(1)}(t) = L\rho_N^{(1)}(t) + L^E(t)\rho_N^{(0)}(t) \tag{29}$$

As may be checked by direct differentiation, the solutions of these two equations are respectively:

$$\rho_N^{(0)}(t) = e^{-iLt}\rho_N^{(0)}(0) \tag{30}$$

$$\rho_N^{(1)}(t) = \frac{1}{i}\int_0^t \exp\left[-iL(t-t')\right]L^E(t')\rho_N^{(0)}(t')dt' \tag{31}$$

if we take into account that the initial state is independent of the field. Inserting Eq. (30) into Eq. (31), we get the alternative form:

$$\rho_N^{(1)}(t) = \frac{1}{i}\int_0^t dt' \exp\left[-iL(t-t')\right] L^E(t') \exp\left[-iLt'\right] \rho_N^{(0)}(0) \quad (31')$$

However, these formal expressions are of no great help until we know how to operate with the exponential operator, which is very complicated because it involves the full N-body problem with the interactions between the particles. In order to circumvent this difficulty, we shall use a *resolvant technique*:[39] we define a resolvant operator $(L - z)^{-1}$, function of the complex variable z, and write:

$$\exp\left[-iLt\right] = -\frac{1}{2\pi i}\oint_C \frac{\exp\left[-izt\right]}{L - z}\, dz \quad (32)$$

The contour C will always be chosen as a straight line parallel to the real axis in the upper half-plane and a large semi-circle in the lower half-plane: as L is Hermitian, all the singularities of the

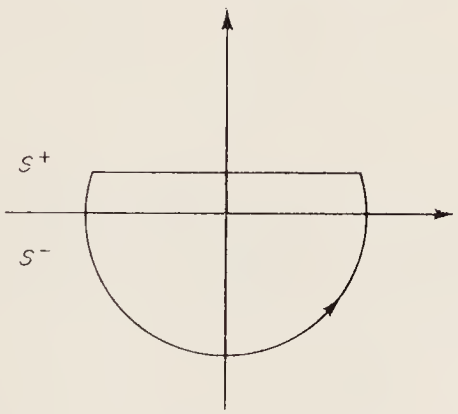

Fig. 1. The complex contour in Eq. (32).

resolvant are on the real axis and are thus included in the contour C. Formula (32) may then be viewed as an operator form of the well-known residue theorem.[31] The resolvant technique furnishes a very elegant method of calculating Eqs. (30) and (31) by perturbation. Indeed, using the operator identity

$$A^{-1} - B^{-1} = A^{-1}(B - A)B^{-1} \quad (33)$$

we may use (13) to write:

$$(L - z)^{-1} = (L_0 + \lambda\delta L - z)^{-1}$$
$$= (L_0 - z)^{-1} + (L_0 - z)^{-1}(-\lambda\delta L)(L - z)^{-1} \tag{34}$$

and by a formal expansion in the coupling parameter λ (supposed convergent), we obtain:

$$(L - z)^{-1} = \sum_{n=0}^{\infty} (L_0 - z)^{-1}[-\lambda\delta L(L_0 - z)^{-1}]^n \tag{35}$$

We notice that the r.h.s. of Eq. (35) only involves the inverse of the unperturbed resolvant $(L_0 - z)^{-1}$. As we have calculated the eigenfunctions and eigenvalues of the operator L_0, this expression has a precise meaning. Indeed, using Eqs. (17), (19), (24), and (25), we get:

$$(L_0 - z)^{-1} = \sum_{kk'} |k\rangle\langle k|(L_0 - z)^{-1}|k'\rangle\langle k'|$$
$$= \sum_{kk'} \frac{1}{k'v - z} |k\rangle\langle k|k'\rangle\langle k'|$$
$$= \sum_{k} |k\rangle \frac{1}{kv - z} \langle k| \tag{36}$$

Before finishing our formal manipulations, we still have to express the distribution functions (30) and (31) in terms of the resolvant operator; it is not difficult to show that (see Eq. (32))

$$\rho_N^{(0)}(t) = -\frac{1}{2\pi i} \oint_C \exp(-izt)dz(L - z)^{-1}\rho_N^{(0)}(0) \tag{37}$$

$$\rho_N^{(1)}(t) = -\frac{1}{2\pi i} \oint_c \exp(-izt)dz\,(L - z)^{-1}\, L^E(L + \omega - z)^{-1}\rho_N^{(0)}(0) \tag{38}$$

B. Fourier Expansion; the Diagram Technique

The unperturbed operator $(L_0 - z)^{-1}$ which appears in Eq. (35) takes a very simple form when expressed in the plane wave

representation (see Eq. (36)). It is thus very natural to expand the distribution function $\rho_N(t)$ in the same eigenfunctions:

$$\rho_N^{(0,1)}(p\,;\,t) = \sum_k \rho_k^{(0,1)}(p\,;\,t)\,\phi_k(r) \tag{39}$$

where

$$\rho_k^{(0,1)}(p\,;\,t) \equiv \langle k|\rho_N^{(0,1)}(p\,;\,t)\rangle = \int dr\,\phi_k^*(r)\rho_N^{(0,1)}(r,\,p\,;\,t) \tag{40}$$

Combining Eqs. (35), (37), (38), and (40), we obtain respectively:

$$\rho_k^{(0)}(p\,;\,t) = \frac{-1}{2\pi i}\oint_C dz\,\exp\,(-izt)\sum_{k'}\sum_{n=0}^{\infty}\langle k|(L_0-z)^{-1}\,[-\lambda\delta L(L_0-z)^{-1}]^n|k'\rangle\,\rho_{k'}^{(0)}\,(p\,;\,0) \tag{41}$$

and

$$\rho_k^{(1)}(p\,;\,t) = \frac{-1}{2\pi i}\oint_C dz\,\exp\,(-izt)\sum_{k'}\sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}\langle k|(L_0-z)^{-1}\,[-\lambda\delta L(L_0-z)^{-1}]^n L^E(L_0+\omega-z)^{-1}\,[-\lambda\delta L(L_0+\omega-z)^{-1}]^{n'}|k'\rangle\rho_{k'}^{(0)}(p\,;\,0) \tag{42}$$

These two expressions are exact; they allow us in principle to calculate the N-particle distribution function at time t (to the first order in the external field) if its initial value is known. This will be our starting point for analyzing electrolytes both at equilibrium and out of equilibrium.

Of course, in many situations, these equations may be simplified. For instance, we may consider the system in the absence of an external field ($\mathbf{E} = 0$) or for uncharged particles ($Z_i = 0$); in these cases, only the first equation remains. On the contrary, we may look at a system which is initially in its equilibrium state $\rho^{\text{eq.}}$; in this case, we have:

$$L\rho^{\text{eq.}} = 0 \tag{43}$$

and the first equation has the trivial solution

$$\rho_k(p\,;\,t) = \rho_k^{\text{eq.}}(p) \tag{44}$$

However, as the technique we shall develop allows us to treat both Eq. (41) and Eq. (42) similarly, we shall generally consider the most general case ($L^E \neq 0$; $\rho_N(0) \neq \rho_N^{\text{eq.}}$).

Until now, our analysis has been purely formal and it is just for mathematical convenience that we have performed the Fourier expansion (39) and (40) for ρ_N. However, we shall see here that this procedure has a very intuitive meaning, which has far-reaching consequences.

(1) *The Fourier coefficients $\rho_k(p\,;t)$ are related to density fluctuations in the system.*

Let us consider, for instance, the *velocity distribution function* $\rho_N(p\,;t)$; it is defined by (see Eq. (40)):

$$\rho_N(p\,;t) = \int dr \rho_N(r, p\,;t) = \Omega^{N/2}\rho_0(p\,;t) \tag{45}$$

It is thus entirely expressed in terms of the zero wave number Fourier coefficient $\rho_0(p\,;t)$. Similarly, the pair correlation function in a spatially homogeneous system is defined by[17]

$$g_2(\mathbf{r}_{12}\,;t) = [\Omega^2 \int dr^{N-2} dp^N \rho_N(r, p\,;t) - 1] \tag{46}$$

We may thus write (see Eq. (39)):

$$g_2(\mathbf{r}_{12}\,;t) = \Omega^{N/2} \sum_{\mathbf{k}\neq 0} \int dp^N \rho_{\mathbf{k}_1-\mathbf{k}_2;\,\{0\}'} \exp -i\mathbf{k}(\mathbf{r}_1 - \mathbf{r}_2) \tag{47}$$

and we thus see that g_2 is entirely determined by Fourier coefficients with two and only two non-vanishing wave numbers.

More generally, deviations from spatial uniformity are expressed by non-vanishing Fourier indices; moreover, all physical quantities of interest are directly expressed with the help of Fourier coefficients involving only a few non-vanishing wave numbers.

In particular, in this monograph, we shall be mainly concerned with the calculation of the pair correlation function (46) for equilibrium situations, from which all other thermodynamic quantities may be calculated, and with the consideration of the electrical current out of equilibrium. This latter is given by:

$$\langle \mathbf{j}(t) \rangle = \sum_i eZ_i \int dr dp \mathbf{v}_i \rho_N(r, p\,;t) \tag{48}$$

or:

$$\langle \mathbf{j}(t) \rangle = \Omega^{N/2} \sum_i eZ_i \int dp \mathbf{v}_i \rho_0(p\,;t) \tag{49}$$

(2) *Due to the translation invariance of the forces, the Fourier matrix elements of the interactions δL and L^E obey very simple selection rules.*

From Eqs. (2), (15), (18), and (23), we get:

$$\langle k|\delta L|k'\rangle = \sum_{i>j} \langle k|\delta L^{ij}|k'\rangle \tag{50}$$

where:

$$\langle k|\delta L^{ij}|k'\rangle = i\frac{1}{\Omega^N}\int dr \exp(-i\sum_l \mathbf{k}_l\mathbf{r}_l)\frac{\partial V}{\partial \mathbf{r}_{ij}}\left(\frac{\partial}{\partial \mathbf{p}_i}-\frac{\partial}{\partial \mathbf{p}_j}\right) \exp\left(i\sum_s \mathbf{k}'_s\mathbf{r}_s\right) \tag{51}$$

which may be directly integrated and gives:

$$\langle k|\delta L^{ij}|k'\rangle = -\frac{1}{\Omega}V_{|\mathbf{k}_i-\mathbf{k}'_i|}(\mathbf{k}_i-\mathbf{k}'_i)\left(\frac{\partial}{\partial \mathbf{p}_i}-\frac{\partial}{\partial \mathbf{p}_j}\right) \delta^{kr}(\mathbf{k}'_i+\mathbf{k}'_j-\mathbf{k}_i-\mathbf{k}_j)\prod_{l\neq ij}\delta^{kr}(\mathbf{k}_l-\mathbf{k}'_l) \tag{52}$$

where V_k is the Fourier transform of the potential:

$$V_k = \int d\mathbf{r}V(r)\exp(i\mathbf{kr}) \tag{53}$$

We see from Eq. (52) that only two wave numbers are modified by an "elementary" interaction δL^{ij} and that the sum of the wave numbers is conserved during a transition:

$$\sum_j \mathbf{k}_j = \sum_j \mathbf{k}'_j \tag{54}$$

In particular, if we start with a spatially homogeneous system, which is such that:

$$\rho_{\{\mathbf{k}\}}(\mathcal{P};0) = 0 \text{ only if } \sum_j \mathbf{k}_j = 0 \tag{55}$$

the system will remain so in the course of time.

Similarly, we have (see Eq. (16)):

$$\langle k|L^E|k'\rangle = -i\sum_i eZ_i\mathbf{E}\langle k|k'\rangle\frac{\partial}{\partial \mathbf{p}_i} = -i\sum_i eZ_i\mathbf{E}\frac{\partial}{\partial \mathbf{p}_i}\delta^{kr}_{k,k'} \equiv L^E\delta^{kr}_{kk'} \tag{56}$$

which is thus a diagonal operator in the Fourier representation.

At this stage, we are in a position which allows us to make very easily a detailed analysis of the exact formal solutions (41) and (42).

Indeed, we have discussed the matrix elements involved in these formulas (see Eqs. (36), (52), and (56)) as well as the physical meaning of the Fourier coefficients $\rho_k(p\,;\,t)$. However, the mathematical expressions are often rather involved and it is convenient, especially in specific applications, to introduce a *diagram technique* in order to represent the various terms of these general formulas.[28] We first notice that in Eqs. (41) and (42), the momenta $\{\mathbf{p}_i\}$ essentially appear as parameters; indeed, according to Eq. (52) only the wave-vectors are *explicitly* modified by the interactions. This is the reason why we shall only represent these wave numbers graphically; it should, however, be kept in mind that the momenta are effectively affected by the interactions through the differential operators $\partial/\partial\mathbf{p}_i$.

At each instant, we represent the state of the system by one horizontal line for each non-vanishing wave number ($\mathbf{k}_i \neq 0$). As an example we show in Fig. 2 a state with $\mathbf{k}_i = -\mathbf{k}_j = \mathbf{k}$.

Fig. 2. The state $\rho_{k_i,k_j=-k_i;\{k_l=0\}'}(p\,;\,t)$.

From Eq. (51), we see that the interactions modify the state of the system: an elementary interaction $\langle k|\delta L|k'\rangle$ brings the system from a state $|k'\rangle$ to a new state $|k\rangle$; the same formula tells us that two wave numbers only are modified in an elementary interaction. One verifies readily that the following six transition schemes are the only possible ones (elementary vertices):

(a)	$\mathbf{k}'_j = \mathbf{k}_i \neq 0$	$\mathbf{k}'_i = \mathbf{k}_j = 0$
(b)	$\mathbf{k}'_i = -\mathbf{k}'_j \neq 0$	$\mathbf{k}_i = \mathbf{k}_j = 0$
(c)	$\mathbf{k}'_i,\ \mathbf{k}'_j,\ \mathbf{k}_i \neq 0$	$\mathbf{k}_j = 0$
(d)	$\mathbf{k}'_i,\ \mathbf{k}_i,\ \mathbf{k}_j \neq 0$	$\mathbf{k}'_j = 0$
(e)	$\mathbf{k}_i = -\mathbf{k}_j \neq 0$	$\mathbf{k}'_i = \mathbf{k}'_j = 0$
(f)	$\mathbf{k}_i,\ \mathbf{k}_j,\ \mathbf{k}'_j,\ \mathbf{k}'_i \neq 0$	

together with the situations obtained by permutations of i and j. The corresponding diagrams are given in Fig. 3.

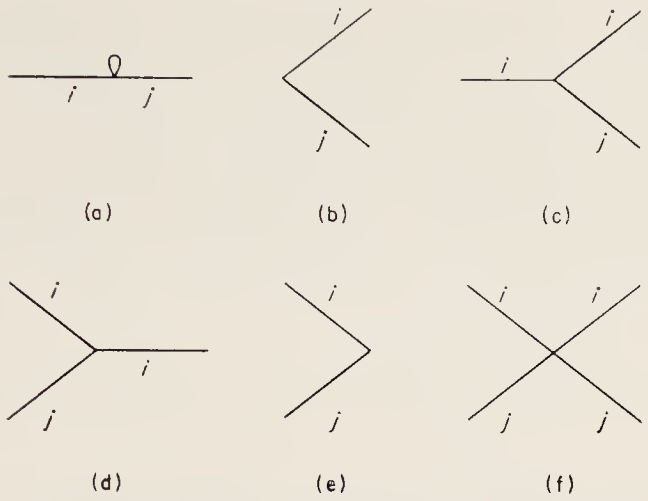

Fig. 3. Elementary vertices.

With these definitions, it is very easy to draw the diagram corresponding to a given term of the expansion (41): reading a contribution from right to left (i.e. in the arrow of time), the lines of the initial state $\rho_{\{\mathbf{k}'\}}(p;0)$ are first represented; then each of the interactions which lead the system to the intermediate states $\{\mathbf{k}''\}$, $\{\mathbf{k}'''\}$. . . are indicated by the corresponding elementary vertex of Fig. 3 until the final state $\{\mathbf{k}\}$ is reached. *These vertices are ordered from right to left.*

As an example, we may consider the second-order term of Eq. (41):

$$\lambda^2\rho_0(p;t) = -\frac{1}{2\pi i}\oint_C dz \exp(-izt)\sum_{\mathbf{k}}\left\langle 0\left|\frac{1}{-z}\right|0\right\rangle\langle 0|-\lambda\delta L^{ij}|\mathbf{k}_i,-\mathbf{k}_j\rangle$$
$$\frac{1}{\mathbf{k}\mathbf{v}_{ij}-z}\langle\mathbf{k}_i,-\mathbf{k}_j|-\lambda\delta L^{ij}|0\rangle\left\langle 0\left|\frac{1}{-z}\right|0\right\rangle\rho_0(p;0) \qquad (57)$$

which is represented by the "cycle" diagram of Fig. 4.

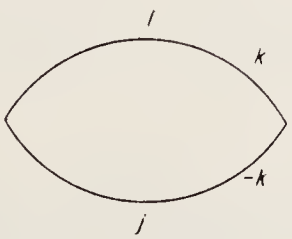

Fig. 4. The cycle.

Reciprocally, one may show that the entire series (41) is generated by drawing all topologically different diagrams; the rules which allow the contribution corresponding to a given graph to be written are very simple but will not be reproduced here.[1,27,31]

For the series (42) giving $\rho^{(1)}(p;t)$, we also need a symbol to represent the external field: we shall use the wavy line of Fig. 5a.

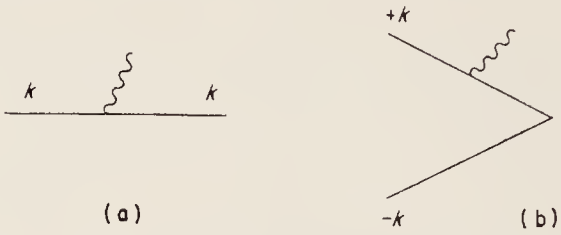

Fig. 5. The transition $\langle \mathbf{k}|L^E|\mathbf{k}\rangle$. (a) The elementary vertex. (b) An example.

For instance, the graph of Fig. 5b corresponds to

$$\rho_{\mathbf{k}_1,-\mathbf{k}_2\{0\}}(p;t) = -\frac{1}{2\pi i}\oint_C dz \exp(-izt)\frac{1}{\mathbf{k}\mathbf{v}_{12}-z}\langle \mathbf{k}_1,-\mathbf{k}_2|L^E|\mathbf{k}_1,-\mathbf{k}_2\rangle$$
$$\frac{1}{\mathbf{k}\mathbf{v}_{12}-z}\langle \mathbf{k}_1,-\mathbf{k}_2|\,-\lambda\delta L^{1,2}|0\rangle\,\frac{1}{-z}\,\rho_0(p;0) \qquad (58)$$

We shall not dwell upon this diagram technique any further and we refer the interested reader to the references above quoted. Applications will be found in the following sections.

C. The Generalized Transport Equation for $\rho^{(0)}(\mathbf{p};\mathbf{t})$: the Approach to Equilibrium

By regrouping the terms of the formal solutions (41) and (42), one may easily derive transport equations for $\rho^{(0)}(t)$ and $\rho^{(1)}(t)$. Here, we shall limit ourselves to the spatially independent elements of these distribution functions [i.e. $\rho_0^{(0)}(t)$ and $\rho_0^{(1)}(t)$ (see Eq. (40))] and we shall merely indicate the main results for $k \neq 0$.

We introduce first a few definitions. The "*diagonal fragment*" $\Psi_{00}(z)$ is the sum of all "irreducible" transitions leading from the state $|0\rangle$ to the same final state; by irreducible, we mean that all intermediate states have non-vanishing wave numbers

($|k\rangle \neq 0$) and this condition will be indicated by a prime in all subsequent formulas. We have thus:

$$\Psi_{00}(z) = \sum_{n=2}^{\infty} (-\lambda)^n \left\langle 0 \left| \delta L \left[\frac{1}{L_0 - z} \delta L \right]^{n-1} \right| 0 \right\rangle' \tag{59}$$

The "*destruction term*" is defined as the sum of all irreducible transitions starting from any initial state $\rho_k(p;0)$ with $k \neq 0$ and ending with the zero wave number state (the "vacuum"):

$$\tilde{\mathscr{D}}_0(z;\rho_k(p;0)) = \sum_{k\neq 0} \sum_{n=1}^{\infty} (-\lambda)^n \left\langle 0 \left| \left(\delta L \frac{1}{L_0 - z} \right)^n \right| k' \right\rangle \rho_k(p;0) \tag{60}$$

Finally, in the calculation of the pair correlation function, we shall also need the so-called "*creation fragment*"; it is defined by:

$$\tilde{C}_{k0}(z) = \sum_{n=1}^{\infty} (-\lambda)^n \left\langle k \left| \left(\frac{1}{L_0 - z} \delta L \right)^n \right| 0 \right\rangle' \tag{61}$$

and thus describes the most general irreducible transition $|0\rangle \rightarrow |k\rangle$.

These three operators, (59), (60), and (61), are schematically indicated by the diagrams of Fig. 6, together with their first few terms in a systematic expansion in λ.

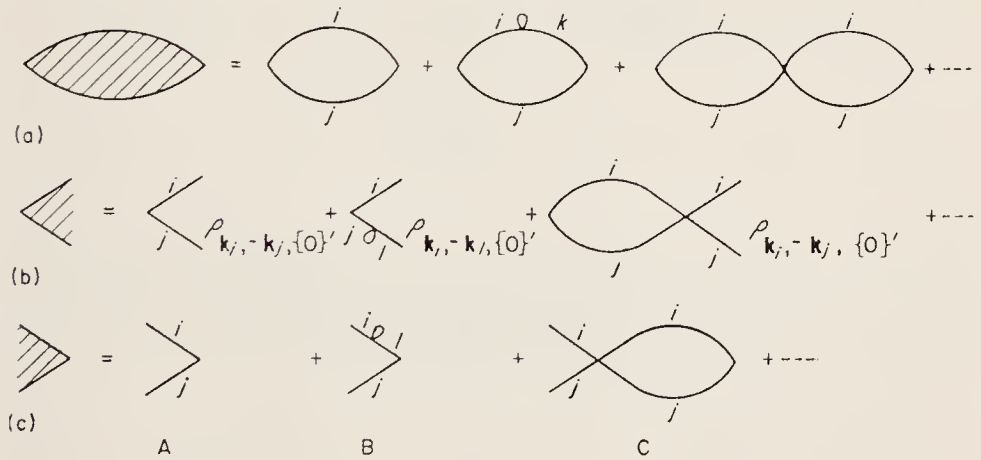

Fig. 6. The basic diagrams of the transport equation for $\rho^{(0)}$. (a) The diagonal fragment. (b) The destruction fragment. (c) The creation fragment.

If we now turn back to the perturbation expansion (41) for $\rho_0^{(0)}(p;t)$, we may obviously express the r.h.s. as the sum of an arbitrary number of diagonal fragments preceded by a destruction fragment. We have indeed identically:

$$\rho_0^{(0)}(p;t) = -\frac{1}{2\pi i}\oint_C \exp(-izt)dz \sum_{k'}\sum_{n=0}^{\infty} \langle 0|(L_0 - z)^{-1} [-\lambda\delta L(L_0 - z)^{-1}]^n |k'\rangle \rho_{k'}(p;0) \tag{62}$$

$$= -\frac{1}{2\pi i}\oint_C dz \exp(-izt)\frac{1}{-z}\sum_{m=0}^{\infty}\left[\frac{\Psi_{00}(z)}{-z}\right]^m [\rho_0(p;0) + \tilde{\mathscr{D}}_0(z;\rho_k(p;0))] \tag{63}$$

In going from Eq. (62) to Eq. (63), we have isolated all the intermediate states $|0\rangle$ and the definitions (59) and (60) have been used. If we now introduce the notations:

$$G_{00}(t) = -\frac{1}{2\pi}\oint_C dz \exp(-izt)\,(i\Psi_{00}(z)) \tag{64}$$

$$\mathscr{D}_0(t;\rho_k(p;0)) = -\frac{1}{2\pi}\oint_C dz \exp(-izt)\tilde{\mathscr{D}}_0(z;\rho_k(p;0)) \tag{65}$$

it is an easy matter to derive a transport equation for $\rho_0^{(0)}(t)$. One first differentiates Eq. (63) with respect to time:

$$\partial_t\rho_0^{(0)}(p;t) = -\frac{1}{2\pi}\oint_C \exp(-izt)dz\Psi_{00}(z)\left[-\frac{1}{z}\sum_{m=0}\left(\frac{\Psi_{00}(z)}{-z}\right)^m (\rho_0(p;0) + \tilde{\mathscr{D}}_0[z;\rho_k(p;0)])\right] - \frac{1}{2\pi}\oint_C \exp(-izt)dz\tilde{\mathscr{D}}_0[z;\rho_k(p;0)] \tag{65'}$$

If we then notice that the bracketed expression in the first integral of (65') is nothing else but the Laplace transform of $\rho_0^{(0)}(p;t)$, we obtain, applying the well-known convolution theorem of Laplace transforms together with the definitions (64) and (65),

$$\partial_t\rho_0^{(0)}(p;t) = \int_0^t dt' G_{00}(t-t')\rho_0^{(0)}(p,t') + \mathscr{D}_0[t;\rho_k^{(0)}(p;0)] \tag{66}$$

We shall not give here a detailed mathematical analysis of this generalized transport equation, derived by Prigogine and

Résibois;[28a] we shall, however, indicate its main physical properties:

(1) The time-dependent operator $G_{00}(\tau)$ describes the most general collision process between the particles in the system; it generalizes to an arbitrary system the well-known Boltzmann collision operator for dilute gases.

It is non-Markoffian and expresses the fact that in strongly coupled systems, account has generally to be taken of the finite duration of the collision process. However, it may be shown that

$$G_{00}(\tau) \to 0, \quad \tau \gg \tau_c \tag{67}$$

where τ_c is a suitably defined collision time which is of the order $a/\bar{v}$ in a dense gas (where a is the radius of the particles and $\bar{v}$ is the average velocity).

(2) The correlations existing at the initial time, which are expressed by $\rho^{(0)}_{k\neq 0}(p\,;0)$ (see Eq. (47)), are *exactly* taken into account in the destruction fragment $\mathscr{D}_0[t\,;\rho_k(p\,;0)]$. Provided these correlations are of molecular origin, one has:

$$\mathscr{D}_0[\tau\,;\rho_k(p\,;0)] \to 0 \quad \tau \gg \tau_c \tag{68}$$

(3) This equation is irreversible if the *thermodynamic limit*

$$N \to \infty, \Omega \to \infty, N/\Omega = C \tag{69}$$

is taken. As a matter of fact, it has to be stressed that the results (67) and (68) are only valid if this same limit is considered.

Then, for times $\tau \gg \tau_c$, the initial condition $\rho^{(0)}_{k\neq 0}(p\,;0)$ completely disappears from (66) and we have:

$$\partial_t \rho^{(0)}_0(p\,;t) = \int_0^t dt' G_{00}(t')\rho^{(0)}_0(t'), \quad t \gg \tau_c \tag{70}$$

It can then be shown[31] that the Maxwellian equilibrium distribution:

$$\rho^{\text{eq.}}_0 = \Omega^{-N/2} \prod_{i=1}^{N} \frac{\exp\left(-p_i^2/2m_i kT\right)}{(2\pi m_i kT)^{3/2}} \tag{71}$$

is the long-time stationary solution of this equation. In other words, one has:

$$\lim_{t\to\infty}\left[\int_0^t dt' G_{00}(t')\right] \rho^{\text{eq.}}_0(p) = 0 \tag{72}$$

For further use, we want to rewrite Eq. (72) in another equivalent form. Using Eq. (64), we have:

$$\frac{1}{2\pi i}\int_0^t dt' \oint_C \exp(-izt')\Psi_{00}(z)dz$$
$$= \frac{1}{2\pi i}\oint_C dz \left(\frac{\exp(-izt)-1}{-iz}\right)\Psi_{00}(z) \tag{73}$$

The time-independent term on the right-hand side of Eq. (73) gives zero because the contour C may be closed in the upper half-plane where $\Psi_{00}(z)$ is everywhere analytic (see Section II-D); we are then left with the time-dependent term, which in the limit $t \to \infty$ only contributes at its pole $z = 0$. From Eqs. (72) and (73), we then get:

$$i\Psi_{00}(i0)\rho_0^{\text{eq.}} = 0 \tag{74}$$

where

$$\Psi_{00}(i0) = \lim_{\varepsilon \to \infty} \Psi_{00}(i|\varepsilon|) \tag{75}$$

Before turning to the transport equation for $\rho_0^{(1)}(t)$, let us add some remarks about the mathematical properties of the basic operators of the theory.

D. Properties of $\Psi_{00}(z)$, $\tilde{\mathscr{D}}_0[z;\ \rho_k(p;\ 0)]$, $\tilde{C}_{k0}(z)$; Equilibrium Correlations

Many interesting properties concerning the analytic behaviour of the quantities $\Psi_{00}(z)$, $\tilde{\mathscr{D}}_0[z;\ \rho_k(p;\ 0)]$ and $\tilde{C}_{k0}(z)$ may be deduced from complex analysis.

We shall not discuss them all in detail here but we shall simply analyze a result which will be important in our further work.

Theorem: $\Psi_{00}(z)$, $\tilde{\mathscr{D}}_0[z;\ \rho_k(p;\ 0)]$, $\tilde{C}_{k0}(z)$ are analytic functions of z in the whole complex plane except for a finite discontinuity along the real axis. For instance, we have two functions $\Psi_{00}^{+}(z)$ and $\Psi_{00}^{-}(z)$ according to whether $\operatorname{Im} z > 0$ or $\operatorname{Im} z < 0$ in Eq. (59); they are analytic in their respective domains of definition, i.e. the first one in the upper half-plane, the second one in the lower

half-plane. Moreover, it is possible to show that $\Psi_{00}^{+}(z)$ has an analytical continuation in the lower half-plane and vice-versa; these continuations have singularities which we shall always assume to be at a finite distance from the real axis.

Let us illustrate this theorem by a simple example; we consider the contribution to $\Psi_{00}(z)$ coming from the cycle of Fig. 4. We have:

$$\Psi_{00}^{(2)}(z) = \lambda^2 \left\langle 0 \left| \delta L \frac{1}{L_0 - z} \delta L \right| 0 \right\rangle' \tag{76}$$

Using the explicit forms (36) and (52) for the matrix elements, we get:

$$\Psi_{00}^{(2)}(z) = -\frac{\lambda^2}{\Omega^2} \sum_{i>j} \sum_{\mathbf{k}} \mathbf{k} V_k \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \frac{1}{\mathbf{k}\mathbf{v}_{ij} - z} \mathbf{k} V_k \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \tag{77}$$

As the next step, we notice that in the limit of an infinite system (65), the spectrum (20) becomes dense and we may use the well-known rule:[3]

$$\sum_{\mathbf{k}} \to \frac{\Omega}{(2\pi)^3} \int d^3k \tag{78}$$

We thus have:

$$\Psi_{00}^{(2)}(z) = -\frac{\lambda^2}{8\pi^3 \Omega} \sum_{i>j} \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \left\{ \int d^3k \mathbf{k} V_k \frac{1}{\mathbf{k}\mathbf{v}_{ij} - z} \mathbf{k} V_k \right\} \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \tag{79}$$

The bracketed expression may always be rewritten (using cylindrical coordinates) in the form:

$$F(z) = \int_{-\infty}^{+\infty} \frac{d\omega f(\omega)}{\omega - z} \tag{80}$$

where we have dropped the vector notation and where $f(\omega)$ is a slowly varying function of its argument (for an explicit example, see Ref. 31).

Integrals of the type (80) are known as *Cauchy integrals* and they have well defined properties.[25]

(1°) $F(z)$ is analytic except on the real axis.

(2°) If we denote by $F^+(z)$ the integral (80) computed for $\text{Im } z < 0$ (S^+), this function is analytic in the upper half-plane. Similarly, we have an analytic function $F^-(z)$ for $\text{Im } z < 0$ (S^-).

(3°) There is a finite discontinuity between these two functions on the real x axis:

$$\lim_{|\varepsilon|,|\varepsilon'|\to 0} F^+(x + i|\varepsilon|) - F^-(x - i|\varepsilon'|) = f(x) \tag{80'}$$

(4°) Both functions $F^+(z)$ and $F^-(z)$ have an analytic continuation in the half-plane complementary to the one where they are defined; these analytical continuations have singularities which are determined by the function $f(z)$. From Eq. (80'), it is a simple matter to verify that if we define:

$$F^+(z) = F^-(z) + f(z),\ z \in S^- \tag{81}$$

$$F^-(z) = F^+(z) - f(z),\ z \in S^+ \tag{82}$$

these two functions are analytical continuations of the original functions. Indeed from Eqs. (80') and (81) we have

$$\begin{aligned} \lim_{|\varepsilon|,|\varepsilon'|\to 0} & F^+(x + i\varepsilon) - F^+(x - i\varepsilon') \\ &= F^+(x + i\varepsilon) - F^-(x - i\varepsilon') - f(x) \\ &= 0 \end{aligned} \tag{83}$$

The properties which we have just quoted are essential in the evaluation of asymptotic formulas of the type (73). Suppose, for example, that we have to compute:

$$I = \lim_{t\to\infty} \frac{1}{2\pi i} \oint_C \frac{\exp(-izt)}{z} F(z) \tag{84}$$

where C is the usual contour of Fig. 1 and $F(z)$ is defined by Eq. (80); we shall moreover suppose that $f(z)$ has a simple pole at $z = z_i \in S^-$.

We first notice that, because of the factor $\exp(-izt)$, the integral along the semi-circle at infinity is vanishing; we may thus formally replace $F(z)$ by $F^+(z)$ on that part of the contour.

Moreover, along the real axis, we are in the upper half-plane and, here also, we need $F^+(z)$. We may thus write:

$$I = \lim_{t\to\infty} \frac{1}{2\pi i} \oint_C \frac{\exp(-izt)}{z} F^+(z) \tag{85}$$

This integral is readily performed by residue; if we use Eq. (81) we have:

$$I = \lim_{t\to\infty} \left[F^+(0) + \frac{\exp(-iz_i t)}{z_i} \operatorname{Res} f(z)|_{z=z_i} \right] \tag{86}$$

$$= F^+(0) \tag{87}$$

This is precisely the form we have derived in Eq. (74).

As another application of this method of asymptotic integration, we shall consider the problem of the Fourier coefficients $\rho_{k\neq 0}^{(0)}(p;t)$ in the limit of long times. As mentioned above, we do not wish to give here a detailed proof of the transport equation for $\rho_k^{(0)}(p;t)$ (see, for instance, Ref. 31). The main result of this analysis is, however, very simple: in the limit of long times $(t \to \infty)$, the correlations are entirely determined by the velocity distribution function $\rho_0^{(0)}(p;t)$. One has:

$$\lim_{t\to\infty} \rho_k^{(0)}(p;t) = \lim_{t\to\infty} \int_0^t dt' \, C_{k0}(t-t')\rho_0^{(0)}(p,t') \tag{88}$$

where

$$C_{k0}(\tau) = \frac{-1}{2\pi} \oint_C dz \exp(-iz\tau)\tilde{C}_{k0}^+(z) \tag{89}$$

As we have discussed, $\tilde{C}_{k0}^+(z)$ is a Cauchy integral and, as a consequence, we immediately have:

$$C_{k0}(\tau) \to 0 \quad \tau \gg \tau_c \tag{90}$$

where τ_c is some characteristic collision time.

Moreover, we have seen that if one waits long enough, the velocity distribution $\rho_0^{(0)}(t)$ tends toward the Maxwellian distribution $\rho_0^{\text{eq.}}$ (see Eq. (71)). We thus have:

$$\lim_{t\to\infty} \rho_k^{(0)}(p;t) = \lim_{t\to\infty} \int_0^t C_{k0}(\tau) d\tau \rho_0^{\text{eq.}} \tag{91}$$

Using Eq. (89) and a calculation similar to (73), we get immediately:

$$\lim_{t\to\infty} \rho_k^{(0)}(p;t) = \tilde{C}_{k0}^{+}(0)\rho_0^{\text{eq.}} \tag{92}$$

This time-independent expression obviously has to be identified with the equilibrium distribution. We thus obtain the following *functional relation between the equilibrium correlations* ($k \neq 0$) *and the velocity distribution:*

$$\rho_k^{\text{eq.}}(p) = \tilde{C}_{k0}^{+}(0)\rho_0^{\text{eq.}}(p) \tag{93}$$

This dynamical formulation of the equilibrium correlations in an interacting system will be the starting point of our analysis of equilibrium electrolytes. Of course, this method gives results analogous to the more usual methods based on the canonical distribution:[40]

$$\rho_k^{\text{eq.}}(p) = \left[\frac{\exp(-\beta H)}{\int dr \int dp \exp(-\beta H)}\right]_k \tag{94}$$

but it has the advantage of being readily extended to non-equilibrium situations. We shall not prove here the equivalence between Eqs. (93) and (94) and we refer the reader to the existing literature (see, for instance, Ref. 31).

E. The Generalized Transport Equation for $\rho_0^{(1)}(p;t)$; the Conductivity Tensor

Let us now turn to the derivation of the transport equation for $\rho_0^{(1)}(p;t)$, which is formally given by Eq. (42). We shall reclassify this latter expansion as for $\rho_0^{(0)}(p;t)$. The only difference is that we have to take into account that an interaction L^E is inserted, at the right of which the propagators are now $(L_0 + \omega - z)^{-1}$.

We thus obtain:

$$\rho_0^{(1)}(p;t) = \frac{-1}{2\pi i}\oint_C \exp(-izt)dz \sum_{k,k'} \sum_{n=0}^{\infty} \sum_{n'=0}^{\infty} \left\langle 0 \left| \frac{1}{L_0 - z}\left(-\lambda\delta L \frac{1}{L_0 - z}\right)^n \right| k \right\rangle \langle k|L^E|k\rangle \left\langle k \left| \frac{1}{L_0 + \omega - z}\left(-\lambda\delta L \frac{1}{L_0 + \omega - z}\right)^{n'} \right| k' \right\rangle \rho_{k'}^{(0)}(p;0) \tag{95}$$

$$\rho_0^{(1)}(p;t) = -\frac{1}{2\pi i}\oint_C \exp(-izt)dz \sum_k \sum_{n=0}^{\infty}\sum_{n'=0}^{\infty}\left(-\frac{1}{z}\right)\left(\frac{\Psi_{00}(z)}{-z}\right)^n$$
$$[\langle 0|L^E|0\rangle\delta_{k,0}^{kr} + \langle 0|\tilde{\mathscr{D}}(z)|k\rangle\langle k|L^E|k\rangle\langle k|\tilde{C}(z-\omega)|0\rangle] \quad (96)$$
$$\left(\frac{1}{-z+\omega}\right)\left(\frac{\Psi_{00}(z-\omega)}{-z+\omega}\right)^{n'}[\rho_0^0(p;0) + \tilde{\mathscr{D}}_0(z-\omega;\rho_{k'}^{(0)}(p;0))]$$

It has to be noted that in Eq. (96) two types of terms appear, corresponding to the diagrams of Fig. 7; in the first class, the

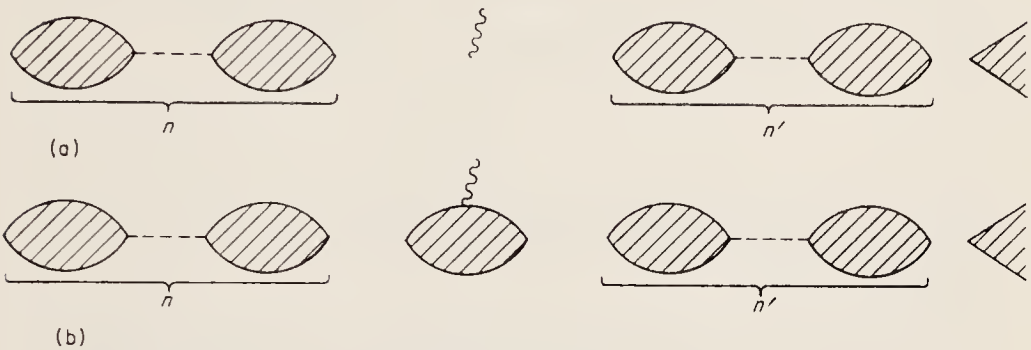

Fig. 7. The two types of contributions to $\rho_0^{(1)}(p;t)$. (a) Free particle acceleration. (b) Correlated particle acceleration.

external field $\langle 0|L^E|0\rangle$ acts on a "vacuum" state, while in the second class, this field acts on mutually correlated particles. This point will be essential for our analysis of the limiting conductance. Also, we have defined the operator $\langle 0|\tilde{\mathscr{D}}(z)|k\rangle$ by analogy with Eq. (60):

$$\langle 0|\tilde{\mathscr{D}}(z)|k\rangle = \sum_{n=0}^{\infty}(-\lambda)^n\left\langle 0\left|\left(\delta L\frac{1}{L_0 - z}\right)^n\right|k\right\rangle' \quad (97)$$

If we introduce the Laplace transform:

$$\rho_0^{(0,1)}(p;t) \equiv -\frac{1}{2\pi i}\oint_C \exp(-izt)dz\tilde{\rho}_0^{(0,1)}(p;z) \quad (98)$$

we may write, from Eqs. (96) and (63):

$$\tilde{\rho}_0^{(1)}(p;z) = \sum_k\sum_{n=0}^{\infty}\left(-\frac{1}{z}\right)\left(\frac{\Psi_{00}(z)}{-z}\right)^n[\langle 0|L^E|0\rangle\delta_{k,0}^{kr}$$
$$+ \langle 0|\tilde{\mathscr{D}}(z)|k\rangle\langle k|L^E|k\rangle\langle k|\tilde{C}(z-\omega)|0\rangle]\tilde{\rho}_0^{(0)}(p;z-\omega) \quad (99)$$

Multiplying both sides by $-z$, we obtain the explicit solution:

$$-z\tilde{\rho}_0^{(1)}(p;z) = [\langle 0|L^E|0\rangle + \sum_{k\neq 0}\langle 0|\tilde{\mathscr{D}}(z)|k\rangle\langle k|L^E|k\rangle$$
$$\langle k|\tilde{C}(z-\omega)|0\rangle]\tilde{\rho}_0^{(0)}(p;z-\omega) + \Psi_{00}(z)\tilde{\rho}_0^{(1)}(p;z) \qquad (100)$$

and by Laplace inversion, we obtain the required transport equation for $\rho_0^{(1)}(p;t)$:

$$\frac{\partial\tilde{\rho}_0^{(1)}}{\partial t}(p;t) + iL^E \exp(-i\omega t)\rho_0^{(0)}(p;t) - i\sum_{k\neq 0}\int_0^t\int_0^{t'} dt'dt''$$
$$\langle 0|\mathscr{D}(t-t')|k\rangle L^E \exp(-iwt')\langle k|C(t'-t'')|0\rangle\tilde{\rho}_0^{(0)}(p;t'')$$
$$= \int_0^t G_{00}(t-t')\rho_0^{(1)}(p;t')dt' \qquad (101)$$

where the time-dependent operators have been defined previously (see Eqs. (64), (65), (89) and (97)) and where we have taken Eq. (56) into account.

Together with Eq. (66), this equation describes exactly the linear response of the system to an external field, with arbitrary initial conditions. Its physical meaning is very simple and may be explained precisely as for Eq. (66);[32] the evolution of the velocity distribution results in two effects: (1) the dissipative collisions between the particles which are described by the same non-Markoffian collision operator $G_{00}(\tau)$ as in the field-free case; and (2) the acceleration of the particles due to the external field. As we are interested in a linear theory, this acceleration only affects the zeroth-order distribution function $\rho_0^{(0)}(p;t)$. It is made up of two parts. First the field acts on the particles when they are non-interacting; this is the second term on the l.h.s. But the situation also exists in which the external force accelerates particles which are mutually interacting: this corresponds to the last term on the l.h.s. In the dilute gas limit, this effect disappears because the duration of the collision is very small. However, in dense systems, it plays an essential role.

Equation (101) is very difficult to solve in general. However, we may simplify it very much if we consider the physical situation of interest: experimentally, one turns on the field at time $t = 0$ and waits for a sufficiently long time, so that all transient effects have disappeared, before measuring the stationary response of

the system. We may thus limit ourselves to the asymptotic solution of Eq. (101) for long times. Then:

(1) We have seen that the zeroth-order velocity distribution function $\rho_0^{(0)}(p;t)$ tends toward its equilibrium value. We thus have:

$$\lim_{t\to\infty} \rho_0^{(0)}(p;t) \to \rho_0^{\text{eq.}}(p) \tag{102}$$

and because of Eq. (68), we may use the asymptotic results (88), (92), and (93):

$$\lim_{t'\to\infty} \int_0^{t'} dt'' C_{k0}(t'-t'')\rho_0^{(0)}(p;t'') = \rho_k^{\text{eq.}}(p) \tag{103}$$

(2) As the field has a definite periodic behavior with frequency ω, we shall also assume that:

$$\rho_0^{(1)}(p;t) \underset{t\to\infty}{=} \rho_{0,\omega}^{(1)}(p) \exp(-i\omega t) \tag{104}$$

where $\rho_{0,\omega}^{(1)}(p)$ is *time-independent.*

Under these circumstances, Eq. (101) becomes:

$$-i\omega\rho_{0,\omega}^{(1)}(p) + iL^E\rho_0^{\text{eq.}}(p) + i\sum_{k\neq 0} \tilde{\mathscr{D}}_{0k}^{+}(\omega)L^E\rho_k^{\text{eq.}}(p) = \Psi_{00}^{+}(\omega)\rho_{0,\omega}^{(1)}(p) \tag{105}$$

where we have used a method of calculation which is now familiar (see Eqs. (73) and (74)):

$$\begin{aligned}
&\lim_{t\to\infty} \int_0^t dt' \langle 0|\mathscr{D}(t-t')|k\rangle L^E \exp(-i\omega t')\rho_k^{\text{eq.}}(p) \\
&= e^{-i\omega t} \lim_{t\to\infty} \int_0^t d\tau \langle 0|\mathscr{D}(\tau)|k\rangle L^E \exp(+i\omega\tau)\rho_k^{\text{eq.}}(p) \\
&= e^{-i\omega t} \lim_{t\to\infty} \int_0^t d\tau \left(-\frac{1}{2\pi}\oint_C \exp[-i(z-\omega)\tau]\tilde{\mathscr{D}}_{0k}(z)dz\right) L^E\rho_k^{\text{eq.}}(p) \\
&= e^{-i\omega t} \lim_{t\to\infty} \left[\frac{1}{2\pi i}\oint \frac{\exp(-izt)}{(z-\omega)} \tilde{\mathscr{D}}_{0k}^{+}(z)dz\right] L^E\rho_k^{\text{eq.}}(p) \\
&= e^{-i\omega t}\, \tilde{\mathscr{D}}_{0k}^{+}(\omega)L^E\rho_k^{\text{eq.}}(p)
\end{aligned} \tag{106}$$

As it stands, the time-independent transport equation (105) still applies to the complete N-particle velocity distribution

function $\rho_N^{(1)}(p)$. This leads to well-known difficulties when the thermodynamic limit (69) is taken: indeed, one obtains all kind of asymptotic behaviors for the various terms appearing in Eq. (105). It is not the place here to discuss these questions but we shall simply indicate a very simple way to solve the problem.[27,28]

What we really need is the electrical current (49), and for this it is sufficient to know the *one-particle velocity distribution function* $\delta\phi_1(\mathbf{p}_i; t)$; indeed, we may write Eq. (49) as:

$$\langle \mathbf{j}(t) \rangle = \sum eZ_i \int d\mathbf{p}_i \mathbf{v}_i \delta\phi_1(\mathbf{p}_i; t) \tag{107}$$

where

$$\delta\phi_1(\mathbf{p}_1; t) = \Omega^{N/2} \int dp^{N-1} \rho_{0,\omega}^{(1)}(p; t) \tag{108}$$

Thus for all practical purposes, it is sufficient to integrate Eq. (105) over $(N-1)$ velocities. Furthermore, it can be shown that the *factorized form*:

$$\rho_{0,\omega}^{(1)}(p) = \Omega^{-N/2} \sum_j \delta\phi_1(\mathbf{p}_j) \prod_{i \neq j=1}^{N} \phi_1^{\text{eq.}}(\mathbf{p}_i) \tag{109}$$

where $\phi_1^{\text{eq.}}(\mathbf{p}_1)$ is the one-particle Maxwellian distribution:

$$\phi_1^{\text{eq.}}(\mathbf{p}_1) = (2\pi m_1 kT)^{-3/2} \exp\left(-p_1^2/2m_1 kT\right) \tag{110}$$

is *rigorous* in the thermodynamic limit (69): it expresses the fact that in the limit of an infinite system, the velocity distributions of each particle are statistically independent. With Eqs. (108) and (109), we readily obtain the transport equation:

$$-i\omega\delta\phi_{1,\omega}(\mathbf{p}_1) + eZ_1\mathbf{E}\frac{\partial}{\partial \mathbf{p}_1}\phi_1^{\text{eq.}}(\mathbf{p}_1) + i\sum_k \int dp^{N-1} \tilde{\mathscr{D}}_{0k}^{+}(\omega) L^E \rho_k^{\text{eq.}}(p)$$
$$= \int dp^{N-1} \Psi_{00}^{+}(\omega) \sum_{j=1}^{N} \delta\phi_{1,\omega}(\mathbf{p}_j) \prod_{i \neq j} \phi^{\text{eq.}}(\mathbf{p}_i) \tag{111}$$

where, we have used for $\rho_k^{\text{eq.}}$ a definition slightly different from (94):

$$\rho_k^{\text{eq.}} = \tilde{C}_{k0}^{+}(0) \prod_{j=1}^{N} \phi^{\text{eq.}}(\mathbf{p}_j) \tag{112}$$

in order to get rid of the unusual normalization factor $\Omega^{N/2}$. Equation (111) will form the basis of our subsequent analysis of

the conductance in electrolytes; it may be shown that, in the thermodynamic limit, the terms of this equation are all finite (see, for instance, Ref. 31 for a similar discussion) but we shall not discuss this point here.

Before closing this chapter, let us note the formal expression for the conductivity tensor per unit volume. We have*

$$\sigma^{\mu\nu}(\omega) = \frac{\langle j^{\mu} \rangle_{\omega}}{\Omega E^{\nu}} = \sum_{\alpha} \frac{eZ_{\alpha}N_{\alpha}}{\Omega} \int \frac{d\mathbf{p}_{\alpha} v_{\alpha}^{\mu} \delta\phi_{1,\omega}(\mathbf{p}_{\alpha})}{E^{\nu}} \tag{113}$$

where α denotes the ionic species. In writing Eq. (113), we have assumed that all the particles of a given species were playing the same role. As $\delta\phi_{1,\omega}(\mathbf{p}_{\alpha})$ is obviously linear in the field, the r.h.s. of Eq. (113) is field-independent, as it should be.

III. EQUILIBRIUM THEORY OF ELECTROLYTES

A. The Problem of Long-Range Coulomb Forces

Let us suppose provisionally that we have a system of N point charges interacting through Coulombic forces:

$$V^{ij} = \frac{e^2 Z_i Z_j}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{114}$$

If the gas of charges (plasma) is sufficiently dilute, we could hope *a priori* that its equation of state would be described by the virial expansion:

$$p = RT[\sum_{\alpha} C_{\alpha} + \sum_{\alpha,\beta} C_{\alpha} C_{\beta} B_{\alpha\beta}(T) + \ldots] \tag{115}$$

where:

$$B_{\alpha\beta}(T) = 2\pi \int_0^{\infty} [1 - \exp(-\beta V^{\alpha\beta})] r^2 dr, \quad \beta = 1/kT \tag{116}$$

is the well-known molecular expression for the second virial coefficient. Here C_{α} denotes the concentration of species α (which is characterized by charge eZ_{α}).

* If we had taken a spatially inhomogeneous field E_q, the connection between the conductivity and the external electric field would be much more complicated than Eq. (113), due to the polarization of the medium.[18] However, for q strictly equal to zero, the system remains spatially homogeneous and Eq. (113) holds.

Formulas (115) and (116) are demonstrated in any textbook on statistical mechanics and we shall not prove them here.[40]

We thus have:

$$B_{\alpha\beta}(T) = 2\pi \int_0^\infty \phi_{\alpha,\beta}(r, T) dr \tag{117}$$

where

$$\phi_{\alpha\beta}(r, T) = r^2[1 - \exp(-\beta V^{\alpha\beta})] \tag{118}$$

Let us discuss this integrand for r respectively small and large.

(1) $r \to 0$. From Eq. (114), we get, if the two particles have charges of the same sign:

$$\underset{r\to 0}{\phi_{\alpha\beta}}(r, T) \simeq -r^2 \left[1 - \exp\left(-\frac{\beta e^2 |Z_\alpha Z_\beta|}{r}\right)\right] \to 0 \tag{119}$$

Due to the Coulombic repulsion, there is of course a vanishing probability of finding the two particles at the same point. On the contrary, if the two charges have opposite sign, we get:

$$\underset{r\to 0}{\phi_{\alpha\beta}}(r, T) \simeq -r^2 \exp\left(+\frac{\beta e^2 |Z_\alpha Z_\beta|}{r}\right) \to -\infty \tag{120}$$

and the two particles have in principle an infinite probability of being at the same point because of the molecular attraction. This in turn leads to an "infinite" reduction of the pressure in Eq. (115)

However, this divergence is not of much significance because:

(1°) "Physical" ions have a finite radius and cannot approach infinitely close to each other.

(2°) At very short distances (of the order of the De Broglie wavelength), quantum effects become very large because the localization energy is getting important.

These two effects tend to introduce a natural cut-off in the integral (116) at a distance r_0, which we shall call, for simplicity, the "radius" of the ions.

We thus see that the short-range divergence is readily eliminated by taking into account only two-body effects; we shall not discuss these any longer in this paper.

(2) $r \to \infty$. Whatever the sign of the charges, we get:

$$\underset{r\to\infty}{\phi_{\alpha\beta}}(r, T) = \beta e^2 Z_\alpha Z_\beta r \to \infty \tag{121}$$

and the integral (117) is thus also divergent at large distances. Although this divergence is physically meaningless, it corresponds nevertheless to a non-trivial difficulty which is encountered with long-range forces. Because the coulombic forces decrease only very slowly with distance, two given molecules are still in interaction when they are very far apart. In this case, the whole idea of the virial expansion (115) becomes meaningless: indeed, it is assumed in the derivation of Eq. (115) that one may decompose the system in clusters involving one, two . . . particles and these

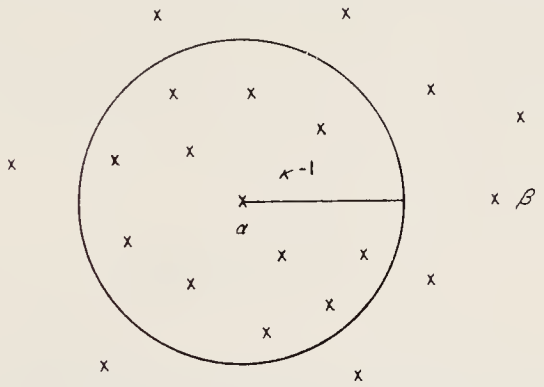

Fig. 8. A typical situation with long-range forces.

clusters have to be well separated in space. Though it is clear that if the molecules α and β were still interacting when they were far apart, we should no longer be allowed to consider them as isolated. We shall have to take into account the other molecules which are between these two ions (see Fig. 8). As we shall see later, these charges distribute themselves in such a manner that the charge on the ion α is "screened" for distances larger than a certain characteristic distance κ^{-1}. This screening effect involves a very large number of particles and we are thus confronted with a typical *collective effect*: the understanding of this collective effect for both equilibrium and non-equilibrium properties of electrolytes will be the basic goal in most of what follows.

B. The Debye-Hückel Theory

As a first step in our understanding of the role of the long-range forces, let us briefly recall the classical theory of Debye–Hückel.[6]

We place an ion α at the origin of our system of coordinates and we look for the probability $n_{\beta\alpha}(r)$ of finding an ion of species β at a distance r. Clearly, this is a very complicated problem because $n_{\beta\alpha}(r)$ will be influenced by the presence of the other ions in the system. We shall, however, make the simplifying assumption that this probability may be written as:

$$n_{\beta\alpha}(r) = C_\beta \exp\left[-\beta Z_\beta e \phi_\alpha(r)\right] \tag{122}$$

where $\phi_\alpha(r)$ is the *total electric potential* acting at the point r. This form (122) is very intuitive and is the basic key to the Debye–Hückel theory; let us however anticipate that it is generally not exact and has been proved to be correct only in the limit of very dilute systems.

Now, we also assume that, *even on a microscopic scale,* Poisson's equation of electrostatics is valid:

$$\nabla^2 \phi_\alpha(r) = -\frac{4\pi}{\varepsilon} \rho_\alpha(r) \tag{123}$$

where $\rho_\alpha(r)$ is the electric charge at point r and ε is the dielectric constant of the solvent (in the case of a plasma, discussed in Section III-A, we have of course $\varepsilon = 1$).

From Eq. (122), we thus have:

$$\nabla^2 \phi_\alpha(r) = -\frac{4\pi e Z_\alpha}{\varepsilon} \delta(\mathbf{r}) - \frac{4\pi e}{\varepsilon} \sum_\beta Z_\beta n_{\beta\alpha}(r) \tag{124}$$

where the first term corresponds to the charge α located at the origin and the second term to the distribution of charges given by Eq. (122). In this formula, we have used the well-known Dirac delta function, which is such that:[3]

$$\int d\mathbf{r} \delta(\mathbf{r} - \mathbf{a}) f(\mathbf{r}) = f(\mathbf{a}) \tag{125}$$

It is remarkable that Eq. (124) itself tells us that the approximation (122) is not rigorous; indeed, the superposition principle of electrostatics indicates that the potential due to a system of charges has to be given by the sum of the potentials created by each single charge: this is not the case for Eq. (124). However, if we limit ourselves to the simple case of a *dilute electrolyte,* we

may suppose that the potential ϕ_α is small; we then expand Eq. (122)

$$n_{\beta\alpha}(r) \simeq C_\beta[1 - \beta Z_\beta e\phi_\alpha(r)] \tag{126}$$

from which we get:

$$\nabla^2\phi_\alpha(r) = \kappa^2\phi_\alpha(r) - \frac{4\pi}{\varepsilon} eZ_\alpha\delta(\mathbf{r}) \tag{127}$$

In deriving Eq. (127), we have used the electroneutrality condition:

$$\sum_\alpha Z_\alpha C_\alpha e = 0 \tag{128}$$

as well as the following definition:

$$\kappa = \left(\frac{4\pi\beta e^2}{\varepsilon}\sum_\beta Z_\beta^2 C_\beta\right)^{1/2} \tag{129}$$

for the so-called *inverse Debye length.*

As can be immediately verified, Eq. (127) is consistent with the superposition theorem.

Equation (127) is most easily solved by the method of Fourier transforms: if we set for any function $\phi(\mathbf{r})$:

$$\phi_\mathbf{k} = \int d\mathbf{r} \exp(i\mathbf{kr})\phi(\mathbf{r}) \tag{130}$$

$$\phi(\mathbf{r}) = \frac{1}{(2\pi)^3}\int d\mathbf{k} \exp(-i\mathbf{kr})\phi_\mathbf{k} \tag{131}$$

we get from Eq. (127):

$$\phi_{\alpha,\mathbf{k}} = \frac{4\pi}{\varepsilon}\frac{eZ_\alpha}{(k^2 + \kappa^2)} \tag{132}$$

and the Fourier inversion gives, in polar coordinates

$$\phi_\alpha(\mathbf{r}) = \frac{1}{(2\pi)^3}\int_0^{2\pi} d\phi \int_{-1}^{+1} dx \int_0^\infty k^2 dk \frac{4\pi}{\varepsilon}\frac{eZ_\alpha}{(k^2 + \kappa^2)} \exp(-ikrx)$$

Straightforward quadratures then lead to

$$\phi_\alpha(\mathbf{r}) = \frac{eZ_\alpha}{\varepsilon r} \exp(-\kappa r) \tag{133}$$

From this result, we get for the pair distribution (126)

$$n_{\beta\alpha}(r) = C_\beta \left[1 - \frac{\beta Z_\alpha Z_\beta e^2}{\varepsilon r} \exp(-\kappa r) \right] \tag{134}$$

and the pair correlation function $g^{\text{eq.}}_{\beta\alpha}(r)$ is (see Eq. (46)):

$$g^{\text{eq.}}_{\beta\alpha}(r) = -\frac{\beta e^2 Z_\alpha Z_\beta}{\varepsilon r} \exp(-\kappa r) \tag{135}$$

As we announced in the preceding paragraph, we see from Eq. (133) that the effective interaction due to the central charge α is screened at a distance of the order κ^{-1}, thus eliminating the divergence difficulty at long distances.

C. Calculation of Thermodynamic Properties

As is well-known, a knowledge of the free energy:

$$F(T, \Omega) = -kT \ln Z_N \tag{136}$$

$$Z_N = \frac{1}{N!} \int d\mathbf{r}_1 \ldots d\mathbf{p}_N \exp(-\beta H_N) \tag{137}$$

allows us to compute all the thermodynamic properties of the system.[40] For instance, the equation of state will be obtained from:

$$p = -\left(\frac{\partial F}{\partial \Omega}\right)_{T,N} \tag{138}$$

We shall now see that $F(T, \Omega)$ may be completely calculated if we know the pair distribution $n_{\alpha\beta}(\mathbf{r})$. Indeed, let us consider the excess free energy

$$F^E(T, \Omega) = -kT \left[\ln \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp(-\beta U_N) - N \ln \Omega \right] \tag{139}$$

which is the difference between the free energy of the real system and the free energy of a corresponding non-interacting system. We may formally go from the latter to the former situation if we introduce a parameter $\bar{\lambda}$:

$$U_{N,\bar{\lambda}} = \bar{\lambda} \sum_{i>j} V^{ij} \tag{140}$$

which we switch on from the free system ($\bar{\lambda} = 0$) to the fully interacting system ($\bar{\lambda} = 1$).

If we define:

$$F^E_{\bar{\lambda}}(T, \Omega) = -kT \left[\ln \int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp(-\beta U_{N,\bar{\lambda}}) - N \ln \Omega \right] \tag{141}$$

we obtain by straightforward differentiation:

$$\frac{\partial F^E}{\partial \bar{\lambda}} = \frac{\int d\mathbf{r}_1 \ldots d\mathbf{r}_N \frac{\partial U_{N,\bar{\lambda}}}{\partial \bar{\lambda}} \exp(-\beta U_{N,\bar{\lambda}})}{\int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp(-\beta U_{N,\bar{\lambda}})} \tag{142}$$

From Eq. (140):

$$\frac{\partial U_{N,\bar{\lambda}}}{\partial \bar{\lambda}} = \frac{U_{N,\bar{\lambda}}}{\bar{\lambda}} \tag{143}$$

and we thus have:

$$\begin{aligned} F^E(T, \Omega) = F^E_{\bar{\lambda}=1}(T, \Omega) &= \int_0^1 d\bar{\lambda} \frac{\partial F^E_{\bar{\lambda}}}{\partial \bar{\lambda}} \\ &= \int_0^1 \frac{d\bar{\lambda}}{\bar{\lambda}} \langle U_{N,\bar{\lambda}} \rangle_{\text{eq.},\bar{\lambda}} \end{aligned} \tag{144}$$

where $\langle U_{N,\bar{\lambda}} \rangle_{\text{eq.},\bar{\lambda}}$ denotes the equilibrium value of the potential energy in the equilibrium situation with a value $\bar{\lambda}$ of the coupling parameter.

From the definition of the pair distribution:

$$n_{12,\bar{\lambda}}(\mathbf{r}_{12}) = N^2 \frac{\int d\mathbf{r}_3 \ldots d\mathbf{r}_N \exp(-\beta U_{N,\bar{\lambda}})}{\int d\mathbf{r}_1 \ldots d\mathbf{r}_N \exp(-\beta U_{N,\bar{\lambda}})} \tag{145}$$

and the pair character of the forces, we get immediately:

$$\langle U_{N,\bar{\lambda}} \rangle_{\text{eq.},\bar{\lambda}} = \frac{1}{2} \sum_{ij} \int d\mathbf{r}_i d\mathbf{r}_j U^{ij}_{\bar{\lambda}} n_{ji,\bar{\lambda}}(\mathbf{r}_{ij})$$

or:

$$\langle U_{N,\bar{\lambda}} \rangle_{\text{eq.},\bar{\lambda}} = \frac{\Omega}{2} \sum_{ij} 4\pi \int_0^\infty r^2 dr U^{ij}_{\bar{\lambda}}(r) n_{ij,\bar{\lambda}}(r) \tag{146}$$

which together with Eq. (144) entirely solves the problem.

In the particular case of electrolytes, we may use Eq. (134) for the pair distribution function. We thus have:

$$\langle U_{N,\bar{\lambda}} \rangle_{\text{eq},\bar{\lambda}} = \frac{\Omega}{2} \sum_{ij} 4\pi \int_0^\infty r^2 dr \, \frac{\bar{\lambda} e^2 Z_i Z_j}{\varepsilon r} \left[1 - \frac{\bar{\lambda} e^2 \beta Z_i Z_j}{\varepsilon r} \exp - (\sqrt{\bar{\lambda}} \kappa r) \right] \tag{147}$$

and using the electroneutrality condition (128), we finally obtain from Eq. (144):

$$F^E = - \frac{\Omega \kappa^3}{8\pi\beta} \int_0^1 \bar{\lambda}^{1/2} d\bar{\lambda}$$

or

$$\frac{F^E(T, \Omega)}{\Omega} = - \frac{2}{3} \frac{\kappa^3 kT}{8\pi} \tag{148}$$

This latter expression allows us to compute all the excess properties of dilute electrolytic solutions; for instance, the excess osmotic pressure is determined by Eq. (138). The most remarkable result is of course that *all these thermodynamic properties are non-analytic functions of the concentration*:

$$\frac{F^E}{\Omega} \sim (\sum_\alpha C_\alpha Z_\alpha^2)^{3/2} \tag{149}$$

while the simplest theory, based on a cluster expansion, generally gives a smaller effect, proportional to C^2.

We shall not dwell any further on the applications of Eq. (148) and its experimental verification (see Refs. 11 and 8, and references quoted in the latter). We just wish to end this section with a remark which will be relevant later: the result (148) could have been obtained formally if we had taken a virial expansion of the type (115) limited to the second order but calculated with an effective potential:

$$V_{ij}^{\text{eff.}}(r) = \frac{e^2 Z_i Z_j}{\varepsilon r} \exp(-\kappa r) \tag{150}$$

which is concentration-dependent, through the inverse Debye length κ. This point will be relevant to some of the approximate models considered in Section V.

D. The Microscopic Theory of Long-Range Coulomb Forces

Since the pioneer work of Mayer, many methods have become available for obtaining the equilibrium properties of plasmas and electrolytes from the general formulation of statistical mechanics. Let us cite, apart from the well-known cluster expansion:[22] the collective coordinates approach, the dielectric constant method (for an excellent summary of these two methods see Ref. 4), and the nodal expansion method.[23]

In order to gain some familiarity with the more elaborate treatment we shall need in considering the transport properties of electrolytes, we shall however follow here a less traditional approach, due to Balescu and Taylor,[2] which is based on the dynamical formulation we developed in Section II.

Let us recall the central formulas we discussed there (see Eqs. (47), (61), and (112)): the equilibrium correlation function is given by:

$$g^{\text{eq.}}(\mathbf{r}_{12}) = \sum_{k \neq 0} \int d\mathbf{p} \rho^{\text{eq.}}_{\mathbf{k},-\mathbf{k}\{0\}'} \exp(-i\mathbf{k}\mathbf{r}_{12}) \tag{151}$$

with

$$\rho^{\text{eq.}}_{\mathbf{k},-\mathbf{k}\{0\}'} = \langle \mathbf{k}, -\mathbf{k}; \{0\}' | \tilde{C}(0) | 0 \rangle \prod_{j=1}^{N} \phi^{\text{eq.}}(\mathbf{p}_j) \tag{152}$$

where $\phi^{\text{eq.}}(\mathbf{p}_j)$ is the Maxwellian distribution (110) and the creation operator

$$\langle \mathbf{k}, -\mathbf{k}, \{0\}' | \tilde{C}(0) | 0 \rangle = \sum_{n=1}^{\infty} (-\lambda)^n \left\langle \mathbf{k}, -\mathbf{k}, \{0\}' \left| \left[\frac{1}{L_0 - i0} \delta L \right]^n \right| 0 \right\rangle' \tag{153}$$

is obtained from Eq.(61) by taking the limit $z \to i0$.

In the case of electrolytes, we have to put an adequate potential in the explicit form (52) of the matrix elements $\langle \mathbf{k} | \delta L^{ij} | \mathbf{k}' \rangle$: We shall always take:

$$V^{ij}(r) = \frac{e^2 Z_i Z_j}{\varepsilon r} \tag{154}$$

and thus we have:

$$V^{(ij)}_k = \frac{4\pi e^2 Z_i Z_j}{\varepsilon k^2} \tag{155}$$

which is most easily verified by noticing that Eq. (154) obeys Poisson's equation (123) with a single charge at the origin, and then taking the Fourier transform of this latter equation.

We have to emphasize immediately that Eqs. (154) and (155) involve a rather drastic approximation about the behavior of electrolytic solutions, which is not always sufficiently pointed out in elementary presentations of the theory.

In Eq. (154), we assume indeed that only the ions ($Z_i \neq 0$) interact with each other and that the resulting interaction is simply the Coulomb potential modified by the zero-frequency dielectric constant ε of the solvent. Of course, in an exact theory, we would have to take explicitly into account the interactions with the solvent, and the dielectric constant itself should come out of the calculation. The proper way of attacking this problem is based on the theory of the "potential of average forces" and is carefully analyzed in H. L. Friedman's monograph.[11] However, the explicit calculations always become exceedingly complicated and, in one way or another, one always has to have recourse to an approximation of the type (154). It amounts to assuming:

(1) that the long-range part of the effective interaction between two ions in a solvent may be completely described by the dielectric constant ε;

(2) that the short-range part of the interactions involving either ions or solvent molecules may be completely neglected. This approximation can be improved by the hypothesis that the ions have a finite radius; however, it can be shown that this generalization does not affect the limiting term of the excess thermodynamic properties (see Eq. (148)) and we shall thus not introduce it here;

(3) that the solvent molecules give rise to no other long-range effect than the introduction of the dielectric constant ε in Eq. (154).

The main reason why we want to make clear the assumptions involved in Eq. (154) is that, in transport problems, the solvent plays a much more important role because it is largely responsible for the dissipation. We shall thus have to improve these assumptions in order to get a satisfactory description of the non-equilibrium limiting laws.

We now come to the explicit evaluation of Eq. (152) when the

potential is given by Eq. (155). Of course, we expect to find divergences in the various terms of the series (153), at least in the limit $\mathbf{k} \to 0$ which corresponds to large distances in configurational space. In order to understand better the nature of these divergences, let us come back for a moment to the Debye–Hückel result (135). In terms of the Fourier transform $g_{\alpha\beta,\mathbf{k}}$, Eq. (135) becomes:

$$g_{\beta\alpha,\mathbf{k}} = \frac{1}{\Omega} \int d\mathbf{r} \exp i\mathbf{kr} \left[- \frac{e^2 \beta Z_\alpha Z_\beta}{\varepsilon r} \exp(-\kappa r) \right] \tag{156}$$

$$= \frac{-4\pi e^2 \beta Z_\alpha Z_\beta}{\Omega \varepsilon (k^2 + \kappa^2)} \tag{157}$$

From Eq. (155), it is clear that we may identify e^2 with our coupling parameter λ, in which case Eq. (157) takes the form:

$$g_{\beta\alpha,\mathbf{k}} \simeq \frac{\lambda\beta}{\Omega(k^2 + \lambda\beta C)} \tag{158}$$

where we have dropped the unimportant constants Z_α, $4\pi\varepsilon$. Saying nothing for the moment about the convergence of the result, we may of course expand Eq. (158) as a power series in λ when $k \neq 0$:

$$g_{\beta\alpha,\mathbf{k}} \simeq - \frac{\lambda\beta}{\Omega k^2} \sum_{n=0}^{\infty} \left(- \frac{\lambda\beta C}{k^2} \right)^n \tag{159}$$

We thus see that the $(n + 1)$th order contribution to the Debye–Hückel result is of order $k^{-(2n+2)} C^n$ and does indeed diverge in the limit of small k.

The procedure we shall follow in deriving an approximate result (exact in the limit of infinite dilution) from our general formula (152) will be exactly opposite to the calculation leading from Eq. (156) to (159):

(1) We first select the class of terms which behave like Eq. (159). For this purpose, it is very convenient to use the diagram technique of Section II.

(2) We then show that this series, which is formally meaningless for small k, may be explicitly summed and gives precisely the Debye–Hückel result (157).

(3) We finally discuss the contributions that have been neglected and indicate that they lead to negligible contributions in the limit of small concentration.

The first part of this program is readily achieved. Indeed, let us consider for example the three diagrams of Fig. 6c (p. 175) for the creation fragment, which we respectively denote by A, B, and C. We have

$$\tilde{C}^{\mathrm{A}}_{k0}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) = \frac{1}{\mathbf{k}\mathbf{v}_{12} - i0}\frac{\mathbf{k}}{\Omega} V_k \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) \quad (160)$$

The differentiation over the momenta is performed and Eq. (155) is used. The result is:

$$\tilde{C}^{\mathrm{A}}_{k0}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) = -\frac{\beta 4\pi e^2 Z_1 Z_2}{\Omega \varepsilon k^2}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) \quad (161)$$

which is precisely of the form (159) with $n = 0$ ($e^2 = \lambda$!).

For the second graph, we get similarly:

$$\tilde{C}^{\mathrm{B}}_{k0}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) = \frac{1}{\Omega^2}\sum_{l\neq 1,2}\frac{1}{\mathbf{k}\mathbf{v}_{12} - i0}\,\mathbf{k}V_k^{(1,l)}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_l}\right)$$
$$\frac{1}{\mathbf{k}\mathbf{v}_{l2} - i0}\,\mathbf{k}V_k^{(l,2)}\left(\frac{\partial}{\partial \mathbf{p}_l} - \frac{\partial}{\partial \mathbf{p}_2}\right)\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) \quad (162)$$

Using Eq. (155) and taking into account the fact that in Eq. (162) we have a sum over $(N - 2) \simeq N$ ions, we see immediately that the order of magnitude of this term is:

$$\tilde{C}^{\mathrm{B}}_{k0}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) \simeq \frac{1}{\Omega}\frac{\lambda\beta}{k^2}\left(\frac{\lambda\beta C}{k^2}\right) \quad (163)$$

i.e. of the form (159) with $n = 1$. We shall not try here to calculate the exact form of Eq. (162) because we shall soon get a general recursion formula for all the graphs of the type (159). On the contrary, it is easily verified that the third graph of Fig. 6c, namely

$$\tilde{C}^{\mathrm{C}}_{k0}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) = \frac{1}{\Omega^2}\sum_{\mathbf{k}'\neq 0}\frac{1}{\mathbf{k}\mathbf{v}_{12} - i0}\,\mathbf{k}'V_{k'}^{(1,2)}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)$$
$$\frac{1}{(\mathbf{k} - \mathbf{k}')\mathbf{v}_{12} - i0}\,(\mathbf{k} - \mathbf{k}')V_{k-k'}^{(1,2)}\left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_2}\right)\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) \quad (164)$$

is not of the class we want to retain because, whatever its k dependence, which we shall discuss later on, it has the magnitude:

$$\tilde{C}^{\mathrm{C}}_{k0}\prod_i \phi^{\mathrm{eq.}}(\mathbf{p}_i) \sim \lambda^2 \quad (165)$$

without the additional C factor which has to be present according to our criterion (159).

More generally, it is very easily seen that because Eq. (159) implies that at each new vertex (one λ factor) a new particle has to appear (which gives a factor $(1/\Omega)\sum_l \sim C$), the most general diagrams we have to retain are the so-called *"ring diagrams"* of Fig. 9: their most obvious characteristic is that *the same wave k runs through the whole diagram.*

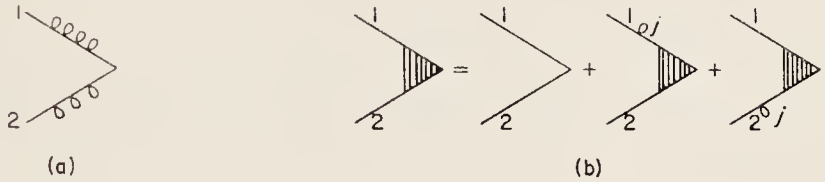

Fig. 9. A ring diagram and the recurrence rule. (a) A ring diagram. (b) The recurrence theorem for ring diagrams.

We could of course write down the explicit form of the general nth order ring diagrams; we prefer however to establish directly an algebraic equation for the whole series and deduce the pair correlation function from its exact solution. Indeed, it is easily verified that the nth order term is derived from the $(n-1)$th one by adding a loop either on the upper or on the lower line. This leads immediately to the "integral" equation of Fig. 9b which we now write in an analytic form.

In accordance with Eq. (152) we write

$$\rho_{\mathbf{k},-\mathbf{k}}^{(12)\text{Ring}}(\not p) = \langle \mathbf{k}, -\mathbf{k}, \{0\}' | \tilde{C}(0) | 0 \rangle_{\text{Ring}} \prod_j \phi^{\text{eq.}}(\mathbf{p}_j) \tag{166}$$

We thus have, using Eq. (161) and Fig. 9b:

$$\rho_{\mathbf{k},-\mathbf{k}}^{(12)\text{Ring}}(\not p) = -\frac{4\pi e^2 \beta Z_1 Z_2}{\Omega \varepsilon k^2} \prod_j \phi^{\text{eq.}}(\mathbf{p}_j) + \frac{1}{\Omega} \sum_{j \neq 1,2} \frac{1}{\mathbf{k}\mathbf{v}_{12} - i0}$$

$$\left[\mathbf{k} \frac{4\pi e^2 Z_1 Z_j}{\varepsilon k^2} \left(\frac{\partial}{\partial \mathbf{p}_1} - \frac{\partial}{\partial \mathbf{p}_j} \right) \rho_{\mathbf{k},-\mathbf{k}}^{(j,2)\text{Ring}} - \mathbf{k} \frac{4\pi e^2 Z_2 Z_j}{\varepsilon k^2} \right.$$

$$\left. \left(\frac{\partial}{\partial \mathbf{p}_2} - \frac{\partial}{\partial \mathbf{p}_j} \right) \rho_{\mathbf{k},-\mathbf{k}}^{(1,j)\text{Ring}} \right] \tag{167}$$

In order to solve Eq. (167), we set the following ansatz:

$$\rho_{\mathbf{k},-\mathbf{k}}^{(1,2)\mathrm{Ring}} = Z_1 Z_2 g_k \prod_j \phi^{\mathrm{eq.}}(\mathbf{p}_j) \tag{168}$$

where g_k is independent of the momenta. This ansatz is justified because we know that the velocity distribution is Maxwellian, even in a system with interactions.

If we introduce Eq. (168) into Eq. (167), we get, after some elementary manipulations:

$$g_k = -\frac{4\pi e^2 \beta}{\Omega \varepsilon k^2} [1 + \Omega \sum_\alpha C_\alpha Z_\alpha^2 g_k] \tag{169}$$

where the greek symbol α denotes the different species and not the different ions.
Thus we have:

$$g_k = -4\pi e^2 \beta / \Omega \varepsilon (k^2 + \kappa^2) \tag{170}$$

where κ^{-1} is the inverse Debye length defined in Eq. (129).

From Eqs. (151) and (168), we then readily obtain:

$$g_{12}^{\mathrm{eq.}}(r) = -\frac{\beta e^2 Z_1 Z_2}{\varepsilon r} \exp(-\kappa r) \tag{171}$$

which is precisely the result of the Debye–Hückel theory.

To summarize, we have just shown that the summation of the infinite class of "ring diagrams" is equivalent to the semi-phenomenological calculations of Debye–Hückel. It will be appreciated that these diagrams are, to any given order, those that involve the largest possible number of different particles: we have here a typical example of a collective effect. Also, it has to be noticed that in the limit $k \to 0$, each term of the expansion is infinite, while the whole sum is well behaved for all wave numbers (see Eq. (169)). This situation is familiar from many problems of statistical mechanics like superfluidity, superconductivity, spin waves, etc. . . ., and gives an *a posteriori* justification to the use of perturbation theory in situations where the coupling between the particles is not really small.

In order to achieve our program, we still have to discuss the non-ring diagrams, which we have completely neglected so far. We want to show that, *although some of these diagrams are actually*

also divergent, they give a smaller contribution than (170) to the pair correlation for small wave numbers (large distances) and small concentrations. We shall, however, not give a complete discussion (see, for example, Ref. 11) and limit ourselves to one single example: the third diagram of Fig. 6c, which has already been evaluated in Eq. (164). We have:

$$\tilde{C}^{C}_{k0}\prod_{i=1}^{N}\phi^{\text{eq.}}(\mathbf{p}_i) = \frac{\beta}{\Omega^2}\sum_{k'\neq 0}\frac{1}{\mathbf{k}\mathbf{v}_{12} - i0}\,\mathbf{k}'V^{(12)}_{k'}\left(\frac{\partial}{\partial\mathbf{p}_1} - \frac{\partial}{\partial\mathbf{p}_2}\right) \times \frac{1}{(\mathbf{k}-\mathbf{k}')\mathbf{v}_{12} - i0}\,(\mathbf{k}-\mathbf{k}')\mathbf{v}_{12}V^{(12)}_{k-k'}\prod_i\phi^{\text{eq.}}(\mathbf{p}_i) \quad (172)$$

which we rewrite (see Eqs. (78) and (155)):

$$\tilde{C}^{C}_{k0}\prod_{i=1}^{N}\phi^{\text{eq.}}(\mathbf{p}_i) = \frac{\beta^2}{\Omega 8\pi^3}\left(\frac{4\pi e^2 Z_1 Z_2}{\varepsilon}\right)^2\frac{\mathbf{v}_{12}}{\mathbf{k}\mathbf{v}_{12} - i0} \times\int d\mathbf{k}'\,\frac{\mathbf{k}'}{k'^2}\,\frac{1}{(\mathbf{k}-\mathbf{k}')^2}\prod_{i=1}\phi^{\text{eq.}}(\mathbf{p}_i) \quad (173)$$

We have, however, through elementary operations:

$$\begin{aligned}\mathbf{I}_k &\equiv \int d\mathbf{k}'\,\frac{\mathbf{k}'}{k'^2}\,\frac{1}{(\mathbf{k}-\mathbf{k}')^2}\\ &= \frac{\mathbf{k}}{2}\int d\mathbf{k}'\,\frac{1}{k'^2(k-k')^2}\\ &= -\frac{\mathbf{k}}{2}\frac{\pi}{k}\int_0^\infty\frac{dx}{x}\ln\frac{|1-x|}{|1+x|} = \frac{\pi^3\mathbf{k}}{2k}\end{aligned} \quad (174)$$

Thus:

$$C^{C}_{k0}\prod_{i=1}^{N}\phi^{\text{eq.}}(\mathbf{p}_i) = \frac{\pi^2}{\Omega}\left(\frac{\beta e^2 Z_1 Z_2}{\varepsilon}\right)^2\frac{1}{k}\prod_i\phi^{\text{eq.}}(\mathbf{p}_i) \quad (175)$$

From this result, we may infer two conclusions:

(1) The non-ring contribution (171) does indeed diverge for small wave numbers. However, *this divergence is weaker than for the ring contributions.*

(2) If we wished to add an arbitrary number of loops to this contribution, we would, precisely as in the case discussed above,

introduce a "natural cut-off" at the Debye inverse length, and we would obtain in the limit of small wave number:

$$\lim_{k\to 0} C^{C}_{k0} \prod_i \phi^{\text{eq.}}(\mathbf{p}_i) \xrightarrow{\text{Ring}} \frac{\pi^2}{\Omega} \left(\frac{\beta e^2 Z_1 Z_2}{\varepsilon}\right) \frac{1}{\kappa} \tag{176}$$

This term is smaller than the ring contribution by a factor $\Gamma^{3/2}$, where Γ is the dimensionless parameter (compare with Eqs. (157) and (170)):

$$\Gamma = \frac{e^2 \beta c^{1/3}}{\varepsilon} \ll 1 \tag{177}$$

in the limit of a dilute electrolyte. In this case, the contribution of Eq. (176) to the distribution function will thus be negligible at large distances (small k).

The same discussion may be extended to the other non-ring diagrams and it can then be shown that *the Debye–Hückel theory is exact in the case of high dilution*. We shall, however, not prove this result and refer the reader to the above mentioned literature for more details.

IV. BROWNIAN MOTION THEORY: A MODEL FOR THE ZEROTH-ORDER CONDUCTANCE

We now turn to transport properties of electrolytes. As mentioned above this problem is much more complicated than the equilibrium one because the solvent plays a crucial role in the description of dissipative phenomena. As a matter of fact, no general solution exists to this problem, because the statistical description of the liquid state is still at a very primitive stage.

It is possible however to analyze mathematically well defined models which we hope will give a correct approximation to real physical systems. In this section, we shall be concerned with the simplest case: the zeroth-order conductance of electrolytes in an infinitely dilute solution. We shall describe this situation by assuming that the ions—which are so far from each other that their mutual interaction may be completely neglected—have a very *large mass* with respect to the solvent molecules; we are then confronted with a typical Brownian motion problem.

Since the early work of Langevin, Einstein, and others, Brownian motion has always provoked a great interest. However, until very recently, its understanding still relied on stochastic assumptions and the theory remained largely phenomenological (see the papers collected by Wax[41]). Only with the latest developments of non-equilibrium statistical mechanics has it been possible to analyze Brownian motion from first principles; in 1963, J. Lebowitz and E. Rubin showed that the well-known Fokker–Planck equation for Brownian motion can be derived from the Liouville equation for a heavy particle in a fluid of light particles. Further developments are due to T. H. Davis, P. Résibois, and J. Lebowitz.[20,32]

In this chapter, we shall first make a brief review of the phenomenological aspect of Brownian motion and we shall then show how the general transport equation derived in Section II allows an exact microscopic theory to be developed.

A. Phenomenological Approach to Brownian Motion

Let us consider a Brownian particle (B-particle) characterized by a mass M_α and coordinates $\mathbf{R}_\alpha$ and $\mathbf{u}_\alpha$. If this B-particle were so large that the fluid could be described by a hydrodynamic approximation (without fluctuations), its motion would be described by:

$$\frac{d\mathbf{R}_\alpha}{dt} = \mathbf{u}_\alpha \tag{178}$$

$$\frac{d\mathbf{u}_\alpha}{dt} = -\frac{\zeta_\alpha}{M_\alpha}\,\mathbf{u}_\alpha \tag{179}$$

where ζ_α is the friction coefficient between the B-particle and the fluid in which it is immersed. Equation (179) expresses the well known fact that the friction force is proportional to the velocity of the particle (valid for small $\mathbf{u}_\alpha$).

However, we are interested in situations in which the B-particle is not quite large enough to allow a continuous description of the fluid; in other words, we want to express the fact that, supplementary to the systematic friction force introduced in Eq. (179), we have to consider a fluctuating force (with zero

average) which depends specifically on the coordinates and momenta of the fluid particles; these coordinates will be denoted by $\{N_\tau\}$. We then get, instead of Eq. (179), the well known Langevin equation:

$$\frac{d\mathbf{u}_\alpha}{dt} = -\frac{\zeta_\alpha}{M_\alpha}\mathbf{u}_\alpha + \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) \tag{180}$$

Clearly enough, for a knowledge of this force we would require a complete calculation of the motion of the fluid particles, i.e. the solution of the $(N+1)$-body problem involving the N fluid particles and the B-particle. This point of view will be adopted in Section IV-C but, in the phenomenological theory, stochastic assumptions are made about this force.

They are introduced in the following way.* We define a probability $W(\mathbf{R}_\alpha; \mathbf{u}_\alpha; t)$ of finding the B-particle in $(\mathbf{R}_\alpha, \mathbf{u}_\alpha)$ at time t and a transition probability $\Psi_{\Delta t}(\mathbf{R}_\alpha - \Delta\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; \Delta\mathbf{R}_\alpha; \Delta\mathbf{u}_\alpha)$ of the B-particle going from $(\mathbf{R}_\alpha - \Delta\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha)$ to $(\mathbf{R}_\alpha, \mathbf{u}_\alpha)$ in the time interval Δt. We then assume the following Markov process:

$$\begin{aligned} W(\mathbf{R}_\alpha; \mathbf{u}_\alpha; t + \Delta t) &= \int\int d(\Delta\mathbf{R}_\alpha) d(\Delta\mathbf{u}_\alpha) \Psi_{\Delta t}(\mathbf{R}_\alpha - \Delta\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; \Delta\mathbf{R}_\alpha; \Delta\mathbf{u}_\alpha) \\ &\quad \times W(\mathbf{R}_\alpha - \Delta\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; t) \end{aligned} \tag{181}$$

which is an "obvious" equation, if the concept of a transition probability makes any sense at all.

Provided Δt is sufficiently small, the velocity $\mathbf{u}_\alpha$ in Eq. (178) remains practically constant and we may thus infer the following form for $\Psi_{\Delta t}$:

$$\begin{aligned} \Psi_{\Delta t}(\mathbf{R}_\alpha - \Delta\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; \Delta\mathbf{R}_\alpha; \Delta\mathbf{u}_\alpha) &= \phi_{\Delta t}(\mathbf{R}_\alpha - \Delta\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha) \\ &\quad \times \delta(\Delta\mathbf{R}_\alpha - \mathbf{u}_\alpha \Delta t) \end{aligned} \tag{182}$$

* In order to make clear that this theory is not derived from the Liouville equation, we use here a notation different from the rest of the paper.

which fixes the increment $\Delta\mathbf{R}_\alpha$ for a given $\mathbf{u}_\alpha$. In Eq. (182) we have introduced the Dirac delta function defined in Eq. (125). We thus get:

$$W(\mathbf{R}_\alpha + \mathbf{u}_\alpha \Delta t; \mathbf{u}_\alpha; t + \Delta t)$$
$$= \int d(\Delta\mathbf{u}_\alpha) \phi_{\Delta t}(\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha) W(\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; t) \quad (183)$$

We now suppose that the transition probability $\phi_{\Delta t}$ has an appreciable value only if $\Delta\mathbf{u}_\alpha$ is small; for small Δt we may then expand:

$$W(\mathbf{R}_\alpha + \mathbf{u}_\alpha \Delta t; \mathbf{u}_\alpha; t + \Delta t)$$
$$= W(\mathbf{R}_\alpha; \mathbf{u}_\alpha; t) + \frac{\partial W}{\partial \mathbf{R}_\alpha} \mathbf{u}_\alpha \Delta t + \frac{\partial W}{\partial t} \Delta t + O(\Delta t^2) + \ldots \quad (184a).$$

$$\phi_{\Delta t}(\mathbf{R}_\alpha; \mathbf{u}_\alpha - \Delta\mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha)$$
$$= \phi_{\Delta t}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha) - \frac{\partial \phi}{\partial \mathbf{u}_\alpha} \Delta\mathbf{u}_\alpha + \frac{1}{2!} \frac{\partial^2 \phi}{\partial \mathbf{u}_\alpha^2} \Delta\mathbf{u}_\alpha \Delta\mathbf{u}_\alpha \quad (184b)$$
$$+ O(\Delta\mathbf{u}_\alpha^3) + \ldots$$

If we notice that the conservation of the B-particle implies:

$$\int d(\Delta\mathbf{u}_\alpha) \phi_{\Delta t}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha) = 1 \quad (185)$$

we then immediately get:

$$\frac{\partial W(\mathbf{R}_\alpha; \mathbf{u}_\alpha; t)}{\partial t} + \mathbf{u}_\alpha \frac{\partial W(\mathbf{R}_\alpha; \mathbf{u}_\alpha, t)}{\partial \mathbf{R}_\alpha} + O(\Delta t)$$
$$= -\frac{\partial}{\partial \mathbf{u}_\alpha}\left[W \frac{\langle \Delta\mathbf{u}_\alpha \rangle}{\Delta t}\right] + \frac{1}{2} \frac{\partial}{\partial \mathbf{u}_\alpha^2}\left[W \frac{\langle \Delta\mathbf{u}_\alpha^2 \rangle}{\Delta t}\right] + O\left[\frac{\langle \Delta\mathbf{u}_\alpha^3 \rangle}{\Delta t}\right] \quad (186)$$

In this formula, we have introduced the so-called first and second moment:

$$\langle \Delta\mathbf{u}_\alpha \rangle = \int d(\Delta\mathbf{u}_\alpha) \Delta\mathbf{u}_\alpha \phi_{\Delta t}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha) \quad (187)$$

$$\langle \Delta\mathbf{u}_\alpha^2 \rangle = \int d(\Delta\mathbf{u}_\alpha) \Delta\mathbf{u}_\alpha \Delta\mathbf{u}_\alpha \phi_{\Delta t}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \Delta\mathbf{u}_\alpha) \quad (188)$$

The differential equation (186) describes the evolution of the B-particle once the moments (187) and (188) are known. Clearly, it is only in these latter expressions that the fluid properties

appear, through the determination of the transition probability $\phi_{\Delta t}$; the natural procedure would thus be to calculate $\phi_{\Delta t}$ from Eqs. (178) and (180) and suitable stochastic assumptions about the fluid. We shall however, follow a simpler method which starts from the remark that Eqs. (187) and (188) clearly give the averages of $\Delta \mathbf{u}_\alpha$ and $(\Delta \mathbf{u}_\alpha \Delta \mathbf{u}_\alpha)$ for all possible fluid configurations. We may thus start from Eq. (180):

$$\Delta \mathbf{u}_\alpha = -\frac{\zeta_\alpha}{M_\alpha} \mathbf{u}_\alpha \Delta t + \int_0^{\Delta t} \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) d\tau \tag{189}$$

$$\Delta \mathbf{u}_\alpha \Delta \mathbf{u}_\alpha = \frac{\zeta_\alpha^2}{M_\alpha^2} \mathbf{u}_\alpha \mathbf{u}_\alpha \Delta t^2 - 2 \frac{\zeta_\alpha}{M_\alpha} \mathbf{u}_\alpha \int_0^{\Delta t} \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) d\tau + \int_0^{\Delta t} \int_0^{\Delta t} \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_{\tau'}\}) d\tau d\tau' \tag{190}$$

and average these equations over all fluid configurations (which we denote by $\langle\ \rangle$). We then get:

$$\langle \Delta \mathbf{u}_\alpha \rangle = -\frac{\zeta_\alpha}{M_\alpha} \mathbf{u}_\alpha \Delta t + \int_0^{\Delta t} \langle \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) \rangle d\tau \tag{191}$$

$$\langle \Delta \mathbf{u}_\alpha \Delta \mathbf{u}_\alpha \rangle = \frac{\zeta_\alpha^2}{M_\alpha} \mathbf{u}_\alpha \mathbf{u}_\alpha \Delta t^2 - 2 \frac{\zeta_\alpha \mathbf{u}_\alpha}{M_\alpha} \int_0^{\Delta t} \langle \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) \rangle d\tau + \int_0^{\Delta t} \int_0^{\Delta t} \langle \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_{\tau'}\}) \rangle d\tau d\tau' \tag{192}$$

We now introduce our stochastic assumptions; first, we have:

$$\langle \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\}) \rangle = 0 \tag{193}$$

because, by definition, the average of the fluctuating force is zero. Moreover:

$$\langle \mathbf{A}(\mathbf{R}_\alpha, \mathbf{u}_\alpha; \{N_\tau\}) \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau'\}) \rangle = \mathbf{U} \bar{\zeta}_\alpha \delta(\tau - \tau') \tag{194}$$

where $\mathbf{U}$ is the unit tensor and $\bar{\zeta}_\alpha$ a constant to be determined later. Equation (194) assumes that the system has such a short memory that the average of the product of two fluctuating forces factorizes (see Eq. (193)) except when the two forces act at the same instant.

Finally, we shall also suppose that

$$\langle \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_\tau\})\mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_{\tau'}\}) \ldots \mathbf{A}(\mathbf{R}_\alpha; \mathbf{u}_\alpha; \{N_{\tau^n}\})\rangle = 0 \text{ if } n > 1 \quad (195)$$

which justifies the neglect of the higher-order terms in Eq. (186). This assumption will be made clearer in our microscopic approach of Section IV-C.

From Eqs. (193) and (194), we get:

$$\langle \Delta\mathbf{u}_\alpha \rangle = -\frac{\zeta_\alpha}{M_\alpha}\mathbf{u}_\alpha \Delta t \quad (196)$$

$$\langle \Delta\mathbf{u}_\alpha \Delta\mathbf{u}_\alpha \rangle = \frac{\zeta_\alpha^2}{M_\alpha^2}\mathbf{u}_\alpha\mathbf{u}_\alpha \Delta t^2 + \mathbf{U}\bar{\zeta}_\alpha \Delta t \quad (197)$$

from which Eq. (186) becomes, in the limit $\Delta t \to 0$:

$$\frac{\partial W}{\partial t} + \mathbf{u}_\alpha \frac{\partial W}{\partial \mathbf{R}_\alpha} = \frac{\partial}{\partial \mathbf{u}_\alpha}\left(\frac{\zeta_\alpha}{M_\alpha}\mathbf{u}_\alpha W\right) + \frac{1}{2}\frac{\partial}{\partial \mathbf{u}_\alpha^2}(\bar{\zeta}_\alpha \mathbf{U} W) \quad (198)$$

where the coefficient $\bar{\zeta}_\alpha$ is still to be determined.

We shall calculate it from general considerations on ergodicity: indeed, we know that any distribution W tends, after a sufficiently long time, toward the Maxwellian velocity distribution:

$$W^{\text{eq.}} = (2\pi M_\alpha kT)^{3/2} \exp(-M_\alpha u_\alpha^2/2kT) \quad (199)$$

$W^{\text{eq.}}$ has thus to be a time-independent solution of Eq. (198); this gives:

$$0 = \frac{\partial}{\partial \mathbf{u}_\alpha}\frac{\zeta_\alpha}{M_\alpha}\mathbf{u}_\alpha W^{\text{eq.}} + \frac{1}{2}\nabla^2_{\mathbf{u}\alpha}\bar{\zeta}_\alpha W^{\text{eq.}} \quad (200)$$

$$\left(\frac{\zeta_\alpha}{M_\alpha} - \frac{\bar{\zeta}_\alpha M_\alpha}{2kT}\right)\frac{\partial}{\partial \mathbf{u}_\alpha}\mathbf{u}_\alpha \exp\left(-\frac{M_\alpha u^2{}_\alpha}{2kT}\right) = 0 \quad (201)$$

As this equality has to be satisfied for all values of $\mathbf{u}_\alpha$, we have

$$\bar{\zeta}_\alpha = 2kT\zeta_\alpha/M_\alpha^2 \quad (202)$$

Equation (198) then becomes the well known *Fokker–Planck equation*:

$$\frac{\partial W}{\partial t} + \mathbf{u}_\alpha \frac{\partial W}{\partial \mathbf{R}_\alpha} = \frac{\zeta_\alpha}{M_\alpha}\frac{\partial}{\partial \mathbf{u}_\alpha}\left[\mathbf{u}_\alpha + \frac{kT}{M_\alpha}\frac{\partial}{\partial \mathbf{u}_\alpha}\right] W \quad (203)$$

The properties of this equation have been thoroughly studied and it has been used in many different contexts.[41] We shall however not discuss it any further here except for the specific application we have in mind, i.e. electrolytic conductance.

B. Zeroth-Order Conductance in the Brownian Approximation

Let us now suppose that each ion in the electrolyte solution may be described by a distribution function $W_i = W(\mathbf{R}_i, \mathbf{u}_i; t)$ which obeys the Fokker–Planck equation (203).

If we now consider a system which is homogeneous at the initial time ($\partial W_i/\partial \mathbf{R}_\alpha = 0$) and if we switch on a constant electric field $\mathbf{E}$, it is not difficult to show that the only modification of Eq. (203) is the introduction of an acceleration term due to this field. We thus have:

$$\frac{\partial W_i}{\partial t} + \frac{Z_i e}{M_i}\mathbf{E}\,\frac{\partial W_i}{\partial \mathbf{u}_i} = \frac{\zeta_i}{M_i}\frac{\partial}{\partial \mathbf{u}_i}\left[\mathbf{u}_i + \frac{kT}{M_i}\frac{\partial}{\partial \mathbf{u}_i}\right] W_i \tag{204}$$

Of course, precisely as in the general case discussed in Section II, we expect that, for long times, we shall have:

$$W_i(t) = W_i^{\text{eq.}} + \delta W_i(t) \tag{205}$$

$$\delta W_i(t) \underset{t\to\infty}{\longrightarrow} \delta W_i \sim E \tag{206}$$

i.e. the system tends toward a stationary state with a linear deviation from equilibrium.

Equation (204) then reduces to:

$$Z_i e\mathbf{E}\,\frac{\partial W_i^{\text{eq.}}}{\partial \mathbf{u}_i} = \zeta_i \frac{\partial}{\partial \mathbf{u}_i}\left[\mathbf{u}_i + \frac{kT}{M_i}\frac{\partial}{\partial \mathbf{u}_i}\right]\delta W_i \tag{207}$$

and the electric current transported by ion i is:

$$\mathbf{j}_i^{(0)} = \int d\mathbf{u}_i e Z_i \mathbf{u}_i \delta W_i(\mathbf{u}_i) \tag{208}$$

In order to compute Eq. (208), let us multiply Eq. (207) by $\mathbf{u}_i$ and integrate over the velocity; we then immediately have:

$$-Z_i e\mathbf{E} = -\int d\mathbf{u}_i \zeta_i \mathbf{u}_i \delta W_i \tag{209}$$

and from Eq. (208), we get:

$$\mathbf{j}_i^{(0)} = Z_i^2 e^2 \mathbf{E}/\zeta_i \tag{210}$$

As we have supposed here that the ions were mutually independent, the total current is given by:

$$\mathbf{J}^{(0)} = \sum_i \frac{Z_i^2 e^2 \mathbf{E}}{\zeta_i} \tag{211}$$

and we arrive at the following result for the conductivity per unit volume:

$$\sigma^{(0)} = \sum_\alpha \frac{Z_\alpha^2 e^2 C_\alpha}{\zeta_\alpha} \tag{212}$$

where the sum is over the various species α.

If we know the friction coefficients ζ_α, we thus have an explicit formula for the conductivity coefficient. In particular, it is often assumed that ζ_α is determined by the well-known Stokes formula:

$$\zeta_\alpha = 6\pi\eta R_\alpha \tag{213}$$

where η is the viscosity of the solvent and R_α the radius of ion α. In this case Eq. (212) is entirely determined. However, it is often better to determine ζ_α by another experiment (a diffusion experiment, for instance, because it is known that the diffusion coefficient $D_\alpha = kT/\zeta_\alpha$).

We see that, provided the Brownian model is satisfactory, the mathematical expression for the zeroth-order conductivity is quite simple. When the interactions between the ions have been accounted for, the resulting expression will be much more involved (see Section V).

C. Microscopic Theory of Brownian Motion

The motion of a heavy ion in a solvent is, of course, a special case of the general transport equation (112), which for simplicity we shall discuss for a time-independent external field ($\omega = 0$):

$$eZ_i \mathbf{E} \frac{\partial}{\partial \mathbf{p}_i} \phi_1^{\text{eq.}}(\mathbf{p}_i) + i \sum_k \int dp^{N-1} \check{\mathscr{D}}_{0k}(0) L^E \rho_k^{\text{eq.}}(p) = \int dp^{N-1} \Psi_{00}^+(0) [\sum_{j=1}^N \delta\phi(\mathbf{p}_j) \prod_{s \neq j}^N \phi^{\text{eq.}}(\mathbf{p}_s)] \tag{214}$$

Two major simplifications occur here.

(1) Because only the B-particle is charged (we shall suppose the B-particle is denoted by the index $1 \equiv \alpha$ thus $eZ_1 \equiv e_\alpha \neq 0$; $eZ_j = 0$ for $j \neq 1$), it is clear that, in the limit of an infinite system, the velocity distribution of the fluid particles will not be affected. This result may be proved rigorously[32] but we shall not demonstrate it here. We thus have:

$$\delta\phi_1(\mathbf{p}_j) = 0 \quad (j = 2 \ldots N) \tag{215}$$

(2) We may explicitly take into account that the mass $m_1 = m_\alpha$ of the B-particle is large with respect to the masses $m_j = m$ $(j > 1)$ of the fluid particles. More precisely, we suppose that, because the deviations from thermal equilibrium are small, the velocities and momenta of interest in Eq. (214) are in the "thermal range" where:

$$v_1 \simeq \langle v_1 \rangle_{\text{eq.}} \sim \sqrt{\frac{kT}{m_\alpha}}, \; p_1 \simeq \langle p_1 \rangle_{\text{eq.}} \sim \sqrt{m_\alpha kT} \tag{216}$$

$$v_j \simeq \langle v_j \rangle_{\text{eq.}} \sim \sqrt{\frac{kT}{m}}, \; p_j \simeq \langle p_j \rangle_{\text{eq.}} \sim \sqrt{mkT} \tag{217}$$

If we introduce the variables

$$\mathbf{v} = \gamma_\alpha^{-1}\mathbf{v}_\alpha \tag{218}$$

$$\mathbf{p} = \gamma_\alpha \mathbf{p}_\alpha \tag{219}$$

where

$$\gamma_\alpha = (m/m\alpha)^{1/2} \ll 1 \tag{220}$$

we see from Eqs. (216) and (217) that all the velocities ($\mathbf{v}$, $\mathbf{v}_2 \ldots \mathbf{v}_N$) as well as all the momenta ($\mathbf{p}$, $\mathbf{p}_2 \ldots \mathbf{p}_N$) are of the same order of magnitude. However, from Eqs. (218) and (219), the operators L^E, $\Psi^+_{00}(0)$ and $\tilde{\mathscr{D}}_{0k}(0)$ now become functions of γ_α; as this parameter is small, we shall make a perturbation expansion around $\gamma_\alpha = 0$ and write:

$$\int dp^{N-1}\Psi^+_{00}(0)\prod_{i\neq 1}\phi^{\text{eq.}}(p_i) = \Omega^{(0)} + \gamma_\alpha\Omega^{(1)} + \gamma_\alpha^2\Omega^{(2)} + \ldots \tag{221}$$

$$\sum_k \int dp^{N-1}\tilde{\mathscr{D}}_{0k}(0)L^E\rho_k^{\text{eq.}}(p) = \gamma_\alpha G^{(1)} + \gamma_\alpha^2 G^{(2)} + \ldots \tag{222}$$

It has to be noted that Eq. (222) is at least of the order γ_α since the operator L^E is proportional to $\partial/\partial \mathbf{p}_\alpha \equiv \gamma_\alpha \partial/\partial \mathbf{p}$: Moreover, it is easy to show that

$$\Omega^{(0)} = \Omega^{(1)} = 0 \tag{223}$$

$$G^{(1)} = G^{(2)} = 0 \tag{224}$$

In order to prove these properties, we decompose in the following way the unperturbed operator L_0 and the perturbation δL, which respectively intervene in Eqs. (55) and (60):

$$L_0 = L_0^f + \gamma_\alpha L_0^I \tag{225}$$

$$\delta L = \delta L^f + \gamma_\alpha \delta L^I \tag{226}$$

where

$$L_0^f = -i \sum_{j=2}^{N} \mathbf{p}_j \frac{\partial}{\partial \mathbf{r}_j} \text{ (fluid unperturbed motion)} \tag{227}$$

$$\gamma_\alpha L_0^I = -i\gamma_\alpha \mathbf{v} \frac{\partial}{\partial \mathbf{R}} \text{ (heavy particle unperturbed motion)} \tag{228}$$

$$\delta L^f = i \sum_{j \neq 1} \frac{\partial u^j(|\mathbf{r}_j - \mathbf{R}|)}{\partial \mathbf{r}_j} \frac{\partial}{\partial \mathbf{p}_j} + i \sum_{i>j>1} \frac{\partial V^{ij}}{\partial \mathbf{r}_{ij}} \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) \tag{229}$$

is just the perturbation the fluid would feel with a Brownian particle fixed at $\mathbf{R}$;

$$\gamma_\alpha \delta L^I = i\gamma_\alpha \sum_{j \neq 1} \frac{\partial u^j(|\mathbf{r}_j - \mathbf{R}|)}{\partial \mathbf{R}} \frac{\partial}{\partial \mathbf{p}} \tag{230}$$

which describes the interaction of the B-particle with the fluid. In these formulas, we have set $\mathbf{r}_\alpha \equiv \mathbf{R}$ in order to introduce clearly the distinction between fluid particles and the B-particle with index α.

From Eqs. (221) and (59), we have thus, for example:

$$\Omega^{(0)} = \int d\mathcal{P}^{N-1} \langle 0| -\delta L^f \sum_n \left(\frac{-1}{L_0^f - i\varepsilon} \delta L^f \right)^n |0\rangle' \prod_{j \neq 1} \phi^{\text{eq.}}(\mathbf{p}_j)$$

and as δL^f involves the differential operator $\left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right)$, it gives zero by direct integration.

The other equations (223) and (224) are similarly proved by using symmetry arguments.

We thus have from Eqs. (214), (215), (221), (222), (223), and (224):

$$\gamma_\alpha e_\alpha \mathbf{E} \frac{\partial}{\partial \mathbf{p}} \phi_1^{\text{eq.}}(\mathbf{p}) + i[\gamma_\alpha^3 G^{(3)} + \ldots]\phi_1^{\text{eq.}}(\mathbf{p}) = i[\gamma_\alpha^2 \Omega^{(2)} + \gamma_\alpha^3 \Omega^{(3)} + \ldots]\delta\phi_1(\mathbf{p})$$

which, to the lowest order in γ_α ($\delta\phi_1(\mathbf{p}) \sim \gamma^{-1}$), reduces to

$$\gamma_\alpha e_\alpha \mathbf{E} \frac{\partial}{\partial \mathbf{p}} \phi_1^{\text{eq.}}(\mathbf{p}) = i\gamma_\alpha^2 \Omega^{(2)} \delta\phi_1(\mathbf{p}) \tag{232}$$

We shall not discuss the higher-order corrections here,[32] but we shall merely analyze the operator $\Omega^{(2)}$. We get from Eq. (59):

$$i\gamma_\alpha^2 \Omega^{(2)} = i\gamma_\alpha^2 \int dp^{N-1} \langle 0| -\delta L^I \left[\frac{1}{L_0^f - i\varepsilon} \sum_{n=0}^{\infty} \left(-\delta L^f \frac{1}{L_0^f - i\varepsilon}\right)^n\right] (-\delta L^I - L_0^I) \sum_{m=0}^{\infty} \left[\frac{1}{L_0^f - i\varepsilon} (-\delta L^f)\right]^m |0\rangle' \rho_0^f \tag{233}$$

where we have used the compact notation:

$$\rho_0^f = \prod_{i=2}^{N} \phi_1^{\text{eq.}}(\mathbf{p}_i) \tag{234}$$

In order to obtain Eq. (233), we have taken into account that $\Omega^{(2)}$ has to begin with $(-\delta L^I)$ otherwise it would give zero precisely as in Eq. (231).

We now use the general theorem indicated in Eq. (94), which reads here:

$$\langle k| \sum_{m=0}^{\infty} \left[\frac{1}{L_0^f - i\varepsilon} (-\delta L^f)\right]^m |0\rangle' \rho_0^f \equiv C_{k0}\rho_0^f + \rho_0^f \delta_{k0}^{kr} = \rho_k^f \tag{235}$$

where ρ_k^f is the Fourier coefficient of the *complete* equilibrium distribution of the fluid in the presence of the fixed B-particle:

$$\rho_k^f = \frac{1}{Z} \int d\mathbf{r} \exp(-i\mathbf{kr}) \exp\left(-\beta \left[\sum_{j=2}^{N} \frac{mv_j^2}{2} + \sum_{ij \geqslant 2} V^{ij} + \sum_{i=2}^{N} u^i\right]\right) \tag{236}$$

where Z is the partition function (see Eq. (137)). We also notice the formal identity:

$$\frac{1}{L_0^f - i\varepsilon}\left[\sum_{n=0}^{\infty}\left(-\delta L^f \frac{1}{L_0^f - i\varepsilon}\right)^n\right] = \frac{1}{L^f - i\varepsilon},\ \varepsilon \to 0$$
$$= i\int_0^{\infty} dt \exp\left[-i(L^f - \varepsilon)t\right] \quad (237)$$

We may thus rewrite Eq. (233) as:

$$i\gamma_\alpha^2\Omega^{(2)} = -\gamma_\alpha^2\int_0^{\infty} dt \int dp^{N-1}\sum_k \langle 0|\delta L^I$$
$$\exp\left[-i(L^f - \varepsilon)t\right](L_0^I + \delta L^I)]|k\rangle \times \rho_k^f \quad (238)$$

We then use the property:

$$L_0^I\rho^f \equiv -i\mathbf{v}\frac{\partial}{\partial \mathbf{R}}\rho^f = -i\beta\mathbf{v}\mathbf{F}^\alpha(\mathbf{R};\{\mathbf{r}_i\})\rho^f \quad (239)$$

where we have introduced the total force acting on the B-particle:

$$\mathbf{F}^\alpha(\mathbf{R};\{\mathbf{r}_i\}) = -\sum_i \frac{\partial u^i(|\mathbf{r}_i - \mathbf{R}|)}{\partial \mathbf{R}} \quad (240)$$

We then obtain, from Eqs. (232) and (238), using the definition of the ket $|k\rangle$:

$$\gamma_\alpha e_\alpha \mathbf{E}\frac{\partial}{\partial \mathbf{p}}\phi_1^{\text{eq.}}(\mathbf{p}) = \gamma_\alpha^2\zeta_\alpha\frac{\partial}{\partial \mathbf{p}}\left[kT\frac{\partial}{\partial \mathbf{p}} + \mathbf{v}\right]\delta\phi_1(\mathbf{p}) \quad (241)$$

where the friction coefficient ζ_α is defined by:

$$\zeta_\alpha = \frac{1}{kT}\int_0^{\infty} dt \langle \mathbf{F}^\alpha \exp\left[-i(L^f - \varepsilon)t\right]\mathbf{F}^\alpha\rangle \quad (242)$$

Here we have used the definition:

$$\langle A\rangle = \int dr^{N-1}dp^{N-1}A\rho^f \quad (243)$$

to denote an average over the fluid distribution ρ^f; it has to be pointed out that Eq. (242) does not depend on the dynamical properties of the B-particle.

Equation (241) is precisely the Fokker–Planck equation deduced above on a purely phenomenological basis; it was first derived

from the Liouville equation by Lebowitz and Rubin.[21] We now see clearly that the justification of the approximation (195) comes from the assumed smallness of γ_α; correction terms involving the autocorrelation of more than two forces would in the present approach come from higher order terms in γ_α.

D. Connection between Microscopic and Macroscopic Theory

In order to complete the demonstration of the equivalence between the two approaches of sections (A) and (C), we need a proof of the equivalence between the definitions (179) and (242) of the friction coefficient ζ_α.

Although the explicit evaluation of ζ_α from Eq. (242) requires the analysis of the N-body problem involved in this formula and will not be given here (see Appendix 4 for a similar problem), the required equivalence is easy to establish on very general grounds.[20]

Consider a B-particle, with coordinates $\mathbf{R}$ at time $t = 0$ and with the *fixed* velocity $\mathbf{v}_\alpha$, moving in a fluid which, at large distances from $\mathbf{R}$, is at equilibrium. After a long time, a stationary

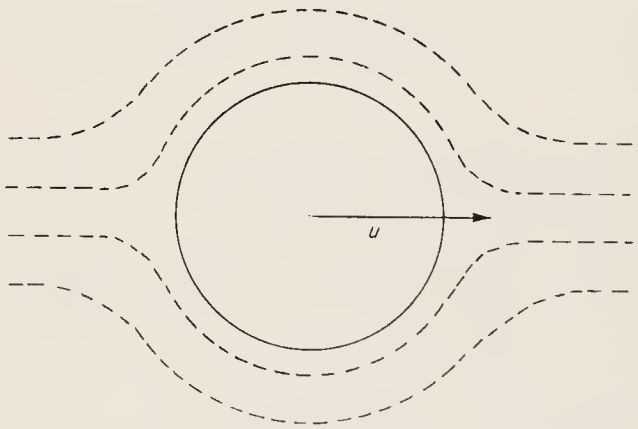

Fig. 10. Field of velocity around the B-particle.

state is realized in a coordinate system moving with the B-particle; let us denote by $\rho^f(\mathrm{st})$ this state of the fluid. The total force acting on the B-particle is then clearly:

$$\langle \mathbf{F}^\alpha \rangle_{\mathrm{st}} = \int dr^{N-1} dp^{N-1} \mathbf{F}^\alpha(\mathbf{R}; \{\mathbf{r}_i\}) \rho^f(\mathrm{st}) \tag{244}$$

We shall now show that this force may be written:

$$\langle \mathbf{F}^{\alpha} \rangle_{\mathrm{st}} = -\zeta_{\alpha} \mathbf{v}_{\alpha} \tag{245}$$

where ζ_{α} is precisely given by Eq. (242); this of course is the required result.

In order to calculate Eq. (244), we immediately start with a system of coordinates fixed on the B-particle and assume that, at the initial time, the fluid is at potential equilibrium with this B-particle while, in our new reference frame, its average velocity is $-\mathbf{v}_{\alpha}$. We thus have:

$$\rho(\mathbf{r}_2 \ldots \mathbf{p}_N; 0) = \frac{1}{Z} \exp\left\{-\beta\left[\sum_{i=2}^{N} \frac{m(\mathbf{v}_i + \mathbf{v}_{\alpha})^2}{2} + \sum_{i>j\geq 2}^{N} V^{ij} + \sum_{i=2}^{N} u^i\right]\right\} \tag{246}$$

If $\beta m v_{\alpha}^2/2 \ll 1$, we may expand Eq. (246) and get:

$$\rho(\mathbf{r}_2 \ldots \mathbf{p}_N; 0) = [1 - \beta(\sum_{i=2}^{N} m\mathbf{v}_i)\mathbf{v}_{\alpha}]\rho^f \tag{247}$$

where ρ^f has been defined in Eq. (236).

As the B-particle remains fixed in our frame of reference, the distribution function at a later time is given by (see Eqs. (227) and (229)):

$$\rho(\mathbf{r}_2 \ldots \mathbf{p}_N; t) = \exp(-iL^f t)\{[1 - \beta\mathbf{v}_{\alpha}(\sum_{i=2}^{N} m\mathbf{v}_i)]\rho^f\} \tag{248}$$

If we now use the identities:

$$\exp(-iL^f t)\rho^f = \rho^f \tag{249}$$

$$\exp(-iL^f t) = 1 + \frac{1}{i}\int_0^t d\tau \exp(-iL^f \tau)L^f \tag{250}$$

which are easy to verify, we have:

$$\rho(\mathbf{r}_2 \ldots \mathbf{p}_N; t) = \rho^f - \beta\mathbf{v}_{\alpha}(\sum_{i=2}^{N} m\mathbf{v}_i)\rho^f - \frac{1}{i}\int_0^t d\tau \exp(-iL^f\tau) \times (L^f \sum_{i=2}^{N} m\mathbf{v}_i)\rho^f \tag{251}$$

The first two terms of Eq. (251) contribute nothing to the average (244) and if we take into account that:

$$L^f \sum_i m\mathbf{v}_i \equiv iF^\alpha(\mathbf{R}; \{\mathbf{r}_i\}) \tag{252}$$

we easily get in the limit $t \to \infty$:

$$\langle \mathbf{F}_\alpha \rangle_{t\to\infty} = -\mathbf{v}_\alpha \int_0^\infty d\tau \int dr^{N-1} \int dp^{N-1} \mathbf{F}^\alpha(\mathbf{R}; \{\mathbf{r}_i\}) \exp(-iL^f\tau) \times \mathbf{F}^\alpha(\mathbf{R}; \{\mathbf{r}_i\})\rho^f \tag{253}$$

which is the required result, provided the integral defined in Eq. (253) converges, which we shall assume.

We have now established the complete equivalence between the two methods of sections (A) and (C). However one question remains unanswered: it is concerned with the applicability of the present approach to the conductance of electrolytes.

Indeed, in order to derive Eq. (212), we had to identify the ions with Brownian particles; strictly speaking, our model is only valid if the ions have a heavy mass with respect to the solvent molecules. Of course, in reality, the situation is very complex: ions and solvent molecules are not point particles interacting through pairwise forces but are much more complicated objects, which have a polarizability, may undergo chemical reactions, and so on. However, it is probably not too bad an approximation to consider a given ion together with its solvating solvent molecules as a single entity, which can very well have, then, a mass large with respect to the solvent molecules. Anyhow, the interest of the present calculations is to furnish solvable models which imitate real systems and where the mathematical approximations involved can be made clear. From now on, we shall thus generally adopt the Brownian model and we shall not discuss its justification any further.

V. THE RELAXATION TERM IN THE LIMITING CONDUCTANCES OF ELECTROLYTES

At a small but finite concentration, the conductivity of an electrolytic solution is no longer given by Eq. (212). Indeed, due

to the long-range character of the Coulombic forces, the interactions between the ions begin to play a role: similarly, the deformation of the fluid around a given ion (see Fig. 10) is felt by the neighboring particles and gives rise to complicated hydrodynamical effects. In this case, we shall see that we have:

$$\sigma(C) = \sigma^0(C) + \delta\sigma \tag{254}$$

$$\delta\sigma(C) = -(A + B)C^{3/2} \tag{255}$$

where C denotes the total concentration, $C = \sum_\alpha C_\alpha$, and A and B are positive constants describing respectively the effect of the electrostatic and of the hydrodynamical interactions between the ions.

More precisely, the A term describes the so-called *relaxation effect*. In the presence of an external field, the stationary Debye cloud around each ion is no longer spherically symmetric because it is unable to adjust itself around the central moving ion. As a consequence, an internal field is created which acts on this central ion and has an opposite sign to the external field. The conductivity, which is determined by the total field, is thus reduced, as indicated by Eq. (255). The hydrodynamical B term expresses the fact that a given ion is slowed down by the solvent molecules which have previously interacted with ions of its Debye cloud; as the charge on this cloud is opposite in sign to the charge on the central ion, these solvent molecules move, on the average, in the direction opposite to the motion of this central ion, which thus "feels" a larger effective friction, and the conductivity is also reduced by this mechanism (*electrophoretic effect*).

In this section, we shall first give a brief review of the phenomenological theory of these effects.[5a,6,26] We shall then show how the methods we have discussed in the previous sections may be extended to derive a microscopic theory of the relaxation effect; the microscopic theory of electrophoresis will be considered in the next section.

A. Macroscopic Theory

Let us define the joint probability $\gamma_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)$ of finding an ion of type α at $\mathbf{r}_\alpha$ and an ion of type $\beta(\beta = \text{or} \neq \alpha)$ at $\mathbf{r}_\beta$; it is normalized to Ω^2:

$$\int d\mathbf{r}_\alpha, d\mathbf{r}_\beta \, \gamma_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t) = \Omega^2 \tag{256}$$

The product of the number of ions α around $\mathbf{r}_\alpha$ and the number of ions β at $\mathbf{r}_\beta$ is then given by $f_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)d\mathbf{r}_\alpha d\mathbf{r}_\beta$, where

$$f_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t) = C_\alpha C_\beta \gamma_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta : t) \tag{257}$$

We shall always focus our attention on these two ions α and β and consider all the others in an average fashion only.

We now define the conditional velocity $\mathbf{w}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)$ of the ion α at $\mathbf{r}_\alpha$, for a given probability $\gamma_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)$.

It is then easy to verify that $f_{\alpha\beta}$, $\mathbf{w}_\alpha$, and $\mathbf{w}_\beta$ are connected by a *continuity equation*

$$\partial_t f_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t) = -[\mathrm{div}_\alpha f_{\alpha\beta}\mathbf{w}_\alpha + \mathrm{div}_\beta f_{\beta\alpha}\mathbf{w}_\beta] \tag{258}$$

which expresses the fact that the time variation of $f_{\alpha\beta}$ is related to the flow of ions α at $\mathbf{r}_\alpha$ and of ions β at $\mathbf{r}_\beta$.

As we want to compute the velocity of ion α independent of the location and of the species of ion β, we shall need:

$$\mathbf{v}_\alpha(\mathbf{r}_\alpha; t) = \frac{\sum_\beta C_\beta \int d\mathbf{r}_\beta \gamma_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)\mathbf{w}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)}{\sum_\beta C_\beta \int d\mathbf{r}_\beta \gamma_{\alpha\beta}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)} \tag{259}$$

from which the total electrical current can then be evaluated. In order to calculate Eq. (259), we obviously need an equation for $\mathbf{w}_\alpha$; this is obtained by noticing that, in quasistationary situations, the total force acting on each ion is vanishing. We thus have a balance between the friction force $\mathbf{F}_\alpha^F$, the electric force $\mathbf{F}_\alpha^E$, and the diffusion force $\mathbf{F}_\alpha^D$.

$$\mathbf{F}_\alpha^E + \mathbf{F}_\alpha^F + \mathbf{F}_\alpha^D = 0 \tag{260}$$

The explicit form of these forces is as follows:

(1) The *friction force* is according to hydrodynamical theory:[12,13,37]

$$\mathbf{F}_\alpha^F = -\zeta_\alpha[\mathbf{w}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta; t) - \mathbf{g}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)] \tag{261}$$

where the friction coefficient ζ_α is given by Stokes law (213) while $\mathbf{g}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)$ denotes the *fluid* velocity at $\mathbf{r}_\alpha$, if we know for sure that ion β is at $\mathbf{r}_\beta$. This fluid velocity may be calculated from hydrodynamics and is given in the present problem by:

$$\mathbf{g}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta; t) = \chi_\beta(\mathbf{r}_{\alpha\beta})\mathbf{w}_\beta(\mathbf{r}_\beta r_\alpha; t) + \sum_\gamma \chi_\gamma(\mathbf{r}_{\alpha\gamma})C_\gamma \int d\mathbf{r}_\gamma \mathbf{w}_\alpha(\mathbf{r}_\gamma, \mathbf{r}_\alpha; t)\gamma_{\alpha\gamma}(\mathbf{r}_\alpha, \mathbf{r}_\gamma; t) \tag{262}$$

where we have treated all the ions, except the given ion β, in an average manner and where the tensor $\boldsymbol{\chi}_\beta$ is known to be:

$$\boldsymbol{\chi}_\beta(\mathbf{r}_{\alpha\beta}) = \frac{3R_\beta}{4r_{\alpha\beta}}\left[\mathbf{U} + \frac{\mathbf{r}_{\alpha\beta} : \mathbf{r}_{\alpha\beta}}{r^2_{\alpha\beta}}\right] + O(r_{\alpha\beta}^{-2}) \tag{263}$$

where $\mathbf{U}$ is the unit tensor and R_β is the radius of ion β; this formula is valid asymptotically for a large separation $\mathbf{r}_{\alpha\beta}$.

(2) The total *electric force* acting on ion α may be written:

$$\mathbf{F}^E_\alpha = Z_\alpha e[\mathbf{E} - \nabla_\alpha \phi_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\alpha; t) - \nabla_\beta \phi_\beta(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)] \tag{264}$$

It is thus the sum of the external field plus the average internal fields created by the given ions α and β together with their respective atmospheres.

It will be assumed that, precisely as in the equilibrium situation, these potentials may be calculated with help of the Poisson equation:

$$\nabla^2 \phi_\alpha(\mathbf{r}, \mathbf{r}_\alpha; t) = -\frac{4\pi e Z_\alpha \delta(\mathbf{r} - \mathbf{r}_\alpha)}{\varepsilon} - \frac{4\pi^e}{\varepsilon}\sum_\gamma Z_\gamma C_\gamma \gamma_{\alpha\gamma} \tag{265}$$

(3) Finally, we have the *diffusion force*,[14] which tends to be opposed to the existing gradient by thermal motion:

$$\mathbf{F}^D_\alpha = -kT\nabla_\alpha \ln \gamma_{\alpha\beta} \tag{266}$$

Equations (257) through (266) provide us with a closed set of equations which allow us, in principle, to calculate $\gamma_{\alpha\beta}$ and $\mathbf{w}_\alpha$. However, an exact solution of these equations is very difficult to obtain and is moreover not very useful. Indeed, we expect our macroscopic description to be valid only at very small ionic concentrations and it is thus not necessary to derive an exact result; only the leading term in an asymptotic expansion at small C will be relevant. The following approximations will thus be used:

(1°) We expand all quantities around their equilibrium value, which corresponds to $\mathbf{E} = 0$, and retain only first-order corrections. For instance:

$$\mathbf{w}_\alpha = \mathbf{w}^{(1)}_\alpha + \ldots \tag{267}$$

$$\gamma_{\alpha\beta} = \gamma^{(0)}_{\alpha\beta} + \gamma^{(1)}_{\alpha\beta} \tag{268}$$

where $\mathbf{w}_\alpha^{(0)} = 0$ (no motion at equilibrium) and (see (135)): (269)

$$\gamma_{\alpha\beta}^{(0)} = 1 - \frac{\beta Z_\alpha Z_\beta e^2}{\varepsilon r_{\alpha\beta}} \exp(-\kappa r_{\alpha\beta}) \tag{270}$$

With these expansions, Eq. (259) gives, in the limit of an infinite volume,

$$\mathbf{v}_\alpha^{(1)} = \frac{\sum_\beta C_\beta \int d\mathbf{r}_\beta \mathbf{w}_\alpha^{(1)}(\mathbf{r}_\alpha, \mathbf{r}_\beta; t)}{\sum_\beta C_\beta} \tag{271}$$

because the correlated part of Eq. (270) gives a negligible contribution in a large system.

From Eqs. (260), (261), (264), and (266), we then obtain immediately:

$$\mathbf{v}_\alpha^{(1)} = \frac{e\mathbf{E}Z_\alpha}{\zeta_\alpha} - \frac{eZ_\alpha}{\zeta_\alpha} \nabla_\alpha \phi_\alpha^{(1)}(0) + \frac{\sum_\beta C_\beta \int d\mathbf{r}_\beta \mathbf{g}_\alpha^{(1)}(\mathbf{r}_\alpha, r_\beta; t)}{\sum C_\beta} \tag{272}$$

Also, the continuity Eq. (258) and the stationary condition (260) allow us to prove in a straightforward manner that, in the time-independent situation, we have:

$$\begin{aligned}
&\left(\frac{kT}{\zeta_\alpha} + \frac{kT}{\zeta_\beta}\right) \nabla_\alpha^2 \gamma_{\alpha\beta}^{(1)} + \gamma_{\alpha\beta}^{(0)} \left(\frac{Z_\alpha e}{\zeta_\alpha} \nabla_\alpha^2 \phi_\beta^{(1)} + \frac{Z_\beta e}{\zeta_\beta} \nabla_\beta^2 \phi_\alpha^{(1)}\right) \\
&\qquad - \left(\frac{eZ_\alpha}{\zeta_\alpha} - \frac{eZ_\beta}{\zeta_\beta}\right) \mathbf{E} \nabla_\alpha \gamma_{\alpha\beta}^{(0)} \\
&= \left\{\left(-\frac{eZ_\alpha}{\zeta_\alpha} \nabla_\alpha \phi_\alpha^{(1)} + \frac{eZ_\beta}{\zeta_\beta} \nabla_\beta \phi_\beta^{(1)}\right) \nabla_\alpha \gamma_{\alpha\beta}^{(1)} - \left(\frac{eZ_\alpha}{\zeta_\alpha} \nabla_\alpha \phi_\alpha^{(0)}\right.\right. \\
&\quad \left. - \frac{eZ_\beta}{\zeta_\beta} \nabla_\beta \phi_\beta^{(0)}\right) \nabla_\alpha \gamma_{\alpha\beta}^{(1)} - \left(\frac{eZ_\alpha}{\zeta_\alpha} \nabla_\alpha^2 \phi_\beta^{(0)} + \frac{eZ_\beta}{\zeta_\beta} \nabla_\beta^2 \phi_\alpha^{(0)}\right) \gamma_{\alpha\beta}^{(1)} \\
&\quad - \left(\frac{eZ_\alpha}{\zeta_\alpha} \nabla_\alpha \phi_\beta^{(0)} - \frac{eZ_\beta}{\zeta_\beta} \nabla_\beta \phi_\alpha^{(0)}\right) \nabla_\alpha \gamma_{\alpha\beta}^{(1)} - \left(\frac{eZ_\alpha}{\zeta_\alpha} \nabla_\alpha \phi_\beta^{(1)}(0)\right. \\
&\quad \left.\left. - \frac{eZ_\beta}{\zeta_\beta} \nabla_\beta \phi_\alpha^{(1)}(0)\right) \nabla_\alpha \gamma_{\alpha\beta}^{(0)}\right\} + (\mathbf{g}_\alpha^{(1)} - \mathbf{g}_\beta^{(1)}) \nabla_\alpha \gamma_{\alpha\beta}^{(0)}
\end{aligned} \tag{273}$$

provided that we take into account that the functions $\gamma_{\alpha\beta}$, $\mathbf{w}_\beta$ only depend on the difference $\mathbf{r}_\alpha - \mathbf{r}_\beta$ and if we note that $\nabla_\alpha \boldsymbol{\chi}_{\alpha\beta} = 0$.

(2°) Equation (273) is still extraordinarily difficult to solve. As we are, however, interested in a limiting law which corresponds to a weak coupling result (see Eq. (171)) we may formally consider the charge e as a smallness parameter; we thus have:

$$\gamma^0_{\alpha\beta} \sim 1,\ \nabla_\alpha \gamma^{(0)}_{\alpha\beta} \sim e^2,\ \phi^{(1)}_\alpha \sim e\gamma^{(1)}_{\alpha\beta} \tag{274}$$

as is verified from Eqs. (265) and (270). It is then easy to check that the lowest-order term in the solution of Eq. (274) is:

$$\phi^{(1)}_\alpha \sim e^2,\ f^{(1)}_{\alpha\beta} \sim e^3 \tag{275}$$

The bracketed expression on the r.h.s. of Eq. (273) is thus at least of order e^4 and may be neglected with respect to the l.h.s., which is of order e^3.

As far as the velocity field term is concerned, it may be verified *a posteriori* that it gives a negligible contribution to the limiting law.* We thus get, using Eq. (265)

$$\left(\frac{kT}{\zeta_\alpha} + \frac{kT}{\zeta_\beta}\right) \nabla^2 \gamma^{(1)}_{\alpha\beta}(\mathbf{r}) - \frac{eZ_\alpha}{\zeta_\alpha} \sum_\gamma \frac{4\pi}{\varepsilon} Z_\gamma C_\gamma \gamma^{(1)}_{\gamma\beta}(\mathbf{r}) - \frac{eZ_\beta}{\zeta_\beta} \sum_\gamma \frac{4\pi}{\varepsilon} Z_\gamma C_\gamma \gamma^{(1)}_{\alpha\gamma}(\mathbf{r}) - \mathbf{E}\left(\frac{eZ_\alpha}{\zeta_\alpha} - \frac{eZ_\beta}{\zeta_\beta}\right) \nabla_\beta \gamma^{(0)}_{\alpha\beta} = 0 \tag{276}$$

where we have used the translational invariance of the problem ($\mathbf{r} = \mathbf{r}_\alpha - \mathbf{r}_\beta$) and the symmetry property $\gamma^{(1)}_{\alpha\beta}(\mathbf{r}) = \gamma^{(1)}_{\beta\alpha}(-\mathbf{r})$.

(3) This latter equation is in a managable form and we may solve it by standard methods. We first set:

$$\gamma^{(1)}_{\alpha\beta} = Z_\alpha Z_\beta e^2 \rho^{(1)}_{\alpha\beta} \tag{277}$$

* To the lowest order, we may neglect all correlations and take $\mathbf{w}^{(1)}_\beta \simeq eZ_\beta \mathbf{E}/\zeta_\beta$ in Eq. (262); in this case the velocity field term in (273) behaves like $\exp(-\kappa r)/r^3$ for large distances, while the inhomogeneous term on the l.h.s.

$$\frac{e\mathbf{E}Z_\alpha}{\zeta_\alpha} \nabla_\alpha \gamma^{(0)}_{\alpha\beta} \sim \frac{\exp(-\kappa r)}{r^2}$$

In the limiting law, all dominant contributions come from large distances precisely as in the equilibrium case; we thus see immediately that the velocity field term may be neglected here because it falls off rapidly to zero as $r \to \infty$.

and we obtain:

$$\left(\frac{kT}{\zeta_\alpha}+\frac{kT}{\zeta_\beta}\right)\nabla^2\rho_{\alpha\beta}^{(1)}-\frac{4\pi}{\varepsilon\zeta_\alpha}\sum_\gamma e^2Z_\gamma^2C_\gamma\rho_{\gamma\beta}^{(1)}$$
$$-\frac{4\pi}{\varepsilon\zeta_\beta}\sum_\gamma e^2Z_\gamma^2C_\gamma\rho_{\alpha\gamma}^{(1)}=-\mathbf{E}\left(\frac{eZ_\alpha}{\zeta_\alpha}-\frac{eZ_\beta}{\zeta_\beta}\right)\nabla_\alpha\frac{\exp(-\kappa r)}{\varepsilon(kT)r} \tag{278}$$

In contrast with the equilibrium case, this equation still depends upon the charges of α and β in a complicated manner. Although methods exist to treat the general case,[8] we shall limit ourselves here to the case of a binary electrolyte, composed of species α and β ($\alpha\neq\beta$). The electroneutrality condition thus reads:

$$C_\alpha Z_\alpha+C_\beta Z_\beta=0 \tag{279}$$

It is furthermore not difficult to prove that:

$$\rho_{\alpha\alpha}^{(1)}=\rho_{\beta\beta}^{(1)}=0,\ \rho_{\alpha\beta}^{(1)}=-\rho_{\beta\alpha}^{(1)} \tag{280}$$

i.e. for equal charges, the atmospheres adjust themselves to their equilibrium values. We are thus left with a single equation:

$$\left(\frac{1}{\zeta_\alpha}+\frac{1}{\zeta_\beta}\right)\nabla^2\rho_{\alpha\beta}^{(1)}-\frac{4\pi}{\varepsilon kT}\left(\frac{e^2C_\alpha Z_\alpha^2}{\zeta_\alpha}+\frac{e^2C_\beta Z_\beta^2}{\zeta_\beta}\right)\rho_{\alpha\beta}^{(1)}$$
$$=-\mathbf{E}\left(\frac{eZ_\alpha}{\zeta_\alpha}-\frac{eZ_\beta}{\zeta_\beta}\right)\nabla\frac{\exp(-\kappa r)}{\varepsilon(kT)r} \tag{281}$$

We may then solve Eq. (280) by a Fourier transformation: using the general definition (130), we obtain immediately:

$$\rho_{\alpha\beta,\mathbf{k}}^{(1)}=\frac{-4\pi i\mathbf{kE}\left(\frac{eZ_\alpha}{\zeta_\alpha}-\frac{eZ_\beta}{\zeta_\beta}\right)}{\varepsilon(kT)^2(k^2+\kappa^2)(k^2+\kappa^2q^2)\left(\frac{1}{\zeta_\alpha}+\frac{1}{\zeta_\beta}\right)} \tag{282}$$

where we have defined:

$$q^2\kappa^2\equiv\frac{4\pi}{\varepsilon kT}\frac{\sum_\mu e^2C_\mu Z_\mu^2\frac{1}{\zeta_\mu}}{\sum_\mu\frac{1}{\zeta_\mu}} \tag{283}$$

By Eq. (279), we also have:

$$q^2 = \frac{\zeta_\beta Z_\alpha - \zeta_\alpha Z_\beta}{(Z_\alpha - Z_\beta)(\zeta_\alpha + \zeta_\beta)} \tag{284}$$

From Poisson's equation (265), we get for the Fourier transform of the potential:

$$-k^2\phi_{\alpha,\mathbf{k}} = -\frac{4\pi e^3}{\varepsilon} Z_\alpha Z_\beta^2 C_\beta \rho^{(1)}_{\beta\alpha,\mathbf{k}} \tag{285}$$

and

$$\nabla_r \phi_\alpha^{(r)}(r)|_{r=0} = -\frac{1}{8\pi^3}\int d\mathbf{k} i\mathbf{k}\phi_{\alpha,\mathbf{k}} \tag{286}$$

From Eqs. (279) through (286), we obtain, after some elementary algebraic manipulations:

$$\nabla_r \phi_\alpha(r)|_{r=0} = \frac{e^2\kappa^2 q^2 |Z_\alpha Z_\beta|}{2\pi^2 \varepsilon k T}\int \frac{d\mathbf{k}\mathbf{k}(\mathbf{k}\mathbf{E})}{k^2(k^2+\kappa^2)(k^2+\kappa^2 q^2)} \tag{287}$$

The integral in Eq. (287) is performed and is equal to $\mathbf{E}2\pi^2/3\kappa(1+q)$. We thus get:

$$\nabla_r \phi_\alpha(r)|_{r=0} = \frac{e^2 q^2 \kappa |Z_\alpha Z_\beta|}{3\varepsilon k T(1+q)}\mathbf{E} \tag{288}$$

According to Eq. (272) this internal field gives a contribution to the velocity of particle α equal to

$$\mathbf{v}_\alpha^{\mathrm{rel}(1)} = -\frac{e\mathbf{E}Z_\alpha}{\zeta_\alpha}\left[\frac{e^2 q^2 \kappa |Z_\alpha Z_\beta|}{3\varepsilon k T(1+q)}\right] \tag{289}$$

which corresponds to the so-called *relaxation effect* (*or internal field effect*).

We still have to compute the velocity field term in Eq. (272), which corresponds to the so-called *electrophoretic effect*. We start from the definition (262) and take for $\mathbf{w}_\varepsilon$ ($\varepsilon = \alpha, \gamma$) the lowest-order approximation:

$$\mathbf{w}_\varepsilon = eZ_\varepsilon \mathbf{E}/\zeta_\varepsilon \tag{290}$$

while $\gamma_{\alpha\beta}$ is approximated by its equilibrium value (270); we thus obtain:

$$\mathbf{g}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta) = \boldsymbol{\chi}_\beta(\mathbf{r}_\alpha - \mathbf{r}_\beta)\frac{eZ_\beta\mathbf{E}}{\zeta_\beta} + \int d\mathbf{r}\left\{\sum_\gamma \frac{C_\gamma eZ_\gamma}{\zeta_\gamma}\boldsymbol{\chi}_\gamma(\mathbf{r})\mathbf{E} - \sum_\gamma \frac{Z_\alpha Z_\gamma^2 e^3 C_\gamma}{\zeta_\gamma \varepsilon kT}\boldsymbol{\chi}_\gamma(\mathbf{r})\mathbf{E}\frac{\exp(-\kappa r)}{r}\right\} \tag{291}$$

The first term in the integral is zero because:

$$\sum_\gamma \frac{C_\gamma eZ_\gamma}{\zeta_\gamma}\boldsymbol{\chi}_\gamma(\mathbf{r})\mathbf{E} = \frac{3}{4}\sum_\gamma \frac{C_\gamma eZ_\gamma}{6\pi\eta}\left(\mathbf{U} + \frac{\mathbf{r}\cdot\mathbf{r}}{r^2}\right)\frac{1}{r}\mathbf{E} \tag{292}$$

which vanishes by electroneutrality.* The second part of the integral is readily evaluated:

$$-\sum_\gamma \frac{Z_\alpha Z_\gamma^2 e^3 C_\gamma}{8\pi\eta\varepsilon kT}\int d\mathbf{r}\exp(-\kappa r)\frac{1}{r^2}\left(\mathbf{U} + \frac{\mathbf{r}\cdot\mathbf{r}}{r^2}\right)\mathbf{E} = -\frac{Z_\alpha e\kappa}{6\pi\eta}\mathbf{E} \tag{293}$$

We thus have:

$$\mathbf{g}_\alpha(\mathbf{r}_\alpha, \mathbf{r}_\beta) = \boldsymbol{\chi}_\beta(\mathbf{r}_\alpha - \mathbf{r}_\beta)\frac{eZ_\beta\mathbf{E}}{\zeta_\beta} - \frac{Z_\alpha e\kappa}{6\pi\eta}\mathbf{E} \tag{294}$$

When inserted in Eq. (272), the first term of Eq. (294) gives zero by an argument similar to that for Eq. (292) and the remaining contribution is:

$$\mathbf{v}_\alpha^{(1)\text{el.}} = -\frac{Z_\alpha e\kappa}{6\pi\eta}\mathbf{E} \tag{295}$$

As was announced at the beginning of this section, both the relaxation and the electrophoretic effects are proportional to $\sqrt{\sum_\alpha C_\alpha}$. More precisely, if we use the definitions (113) and the definition of the current per unit volume:

$$\mathbf{J} = \sum_\alpha C_\alpha Z_\alpha e\mathbf{v}_\alpha \tag{296}$$

* It should be pointed out that this result depends crucially upon the fact that ζ_γ, as given by Stokes law (213), and χ_γ, as defined by Eq. (263), depend on the ion γ through the same parameter R_γ. This condition is essential because otherwise the integral would diverge at large distances.

we obtain from Eqs (289) and (295) the following explicit expressions for the constants A and B introduced in Eq. (255):

$$AC^{3/2} \equiv \sigma^{(0)}(C) \left[\frac{e^2 q^2 \kappa |Z_\alpha Z_\beta|}{3\varepsilon k T (1 + q)} \right] \tag{297}$$

$$BC^{3/2} = \frac{\kappa}{6\pi\eta} \sum_\alpha e^2 Z_\alpha^2 C_\alpha \tag{298}$$

This completes our macroscopic description of the limiting conductance in dilute electrolytes.

B. Formulation of the Microscopic Approach: a Simple Model for Relaxation

For simplicity, we shall discuss the case of a time-independent external field;* the generalized transport equation (111) thus takes the form:

$$eZ_\alpha \mathbf{E} \frac{\partial}{\partial \mathbf{p}_\alpha} \phi_{(1)}^{\text{eq.}}(\mathbf{p}_\alpha) - T_\alpha(\mathbf{p}_\alpha) = \mathscr{C}_\alpha(\delta\phi_j) \tag{299}$$

where we have used an abbreviated notation for the collision term:

$$\mathscr{C}_\alpha(\delta\phi_j) = \int dp^{N-1} \Psi_{00}^{+}(0) [\sum_{j=1}^{N} \delta\phi_1(\mathbf{p}_j) \prod_{i \neq j} \phi_1^{\text{eq.}}(\mathbf{p}_i)] \tag{300}$$

as well as for the effect of the external field during a collision process:

$$T_\alpha(\mathbf{p}_\alpha) = -i \sum_{\mathbf{k}} \int dp^{N-1} \tilde{\mathscr{D}}_{0k}^{+}(0) L^E \rho_k^{\text{eq.}}(p) \tag{301}$$

which is *linear* in the field.

As is clear from its derivation, Eq. (299) is quite general: it is valid whatever the charges, the masses, and the concentrations of the various species in the system. We shall thus specify the case of a binary electrolyte:† we consider a system with N_α

* The generalization to $\omega \neq 0$ offers no difficulty[12,13] but will not be considered here.

† Precisely as in the classical theory, the explicit calculations become very complicated for mixtures of electrolytes, although no new fundamental difficulty arises.

ions with charge eZ_α and mass m_α, N_β ions with charge eZ_β and mass m_β, and N_0 solvent molecules with mass m_0. Furthermore, we suppose that the electrolyte is dilute:

$$C_\alpha = \frac{N_\alpha}{\Omega} \ll C_0 = \frac{N_0}{\Omega}; \quad C_\beta \ll C_0 \tag{302}$$

and that the ions are heavy with respect to the solvent molecules:

$$\gamma_\alpha^2 = \frac{m_0}{m_\alpha} \ll 1, \quad \gamma_\beta^2 = \frac{m_0}{m_\beta} \ll 1 \tag{303}$$

Under the conditions (302) and (303), it is easy to obtain an explicit form for $\mathscr{C}_\alpha(\delta\phi_j)$. Indeed, as a first approximation, we may retain only the collision between a single ion and the solvent molecules; in the limit (303), this term was studied in detail in Section IV and the Fokker–Planck operator was derived:

$$\mathscr{C}_\alpha(\delta\phi_j) \equiv i\square^\alpha(0)\delta\phi_\alpha = \zeta_\alpha \frac{\partial}{\partial \mathbf{p}_\alpha}\left[kT\frac{\partial}{\partial \mathbf{p}_\alpha} + \mathbf{v}_\alpha\right]\delta\phi_\alpha \tag{304}$$

Of course for finite C_μ (and infinitesimal γ_μ), corrections arise which are of two types:

(a) The fluid distribution is perturbed by the presence of a finite number of ions in the solution; we thus have $\delta\phi_1(\mathbf{p}_0) \neq 0$, which introduces supplementary terms in Eq. (300). These corrections may be shown to be at least of order C_μ; indeed, due to electroneutrality, there is no momentum transfer to the system

$$\sum_{i=\alpha,\beta,0} \Delta p_i = \int_0^t \mathbf{E}\Big(\sum_{\mu=\alpha,\beta} eZ_\mu N_\mu\Big)dt = 0 \tag{305}$$

Moreover, in the stationary state, the velocity of each ion is, as a first approximation:

$$\mathbf{v}_\mu = \frac{eZ_\mu \mathbf{E}}{\zeta_\mu} \text{ (see Eq. (210))} \tag{306}$$

Thus the velocity of each solvent molecule is of the order:

$$\mathbf{v}_0 = \frac{\mathbf{p}_0}{m_0} = \frac{1}{N_0}\sum_\nu \frac{eZ_\nu N_\nu \mathbf{E}}{\zeta_\nu} = O(C_\nu) \tag{307}$$

(b) We also have to take into account the mutual dissipation between ions; in the case of a plasma ($N_0 = 0$), this term would be the only one in Eq. (300). Although we shall not evaluate this term exactly, it is easily seen to be of the same order of magnitude as in this latter plasma case, where we know that:

$$\mathscr{C}_\alpha(\delta\phi_\mu) \simeq -\delta\phi_\alpha/\tau_\alpha \tag{308}$$

where we have made the simplest possible "relaxation" approximation, namely:[1,38]

$$1/\tau_\alpha \sim C \ln C \tag{309}$$

The logarithmic dependence in Eq. (309) is, of course, characteristic of dissipation due to screened long-range forces. Provided we are only interested in the $C^{1/2}$ correction (limiting law), we may neglect this term also and we are thus left with the collision operator (304).*

Inserting Eq. (304) into Eq. (299), it is very easy to deduce the following expression for the current, in the limit of a dilute electrolyte (see Eq. (209)):

$$\mathbf{J} = \mathbf{J}_0 + \mathbf{J}_1 \tag{310}$$

with

$$\mathbf{J}_0 = \sum_{\mu=\alpha,\beta} \frac{e^2 Z^2{}_\mu C_\mu}{\zeta_\mu} \mathbf{E} \tag{311}$$

and:

$$\mathbf{J}_1 = \sum_{\mu=\alpha,\beta} \frac{eZ_\mu C_\mu}{\zeta_\mu} \int d^3p \mathbf{p}_\mu T_\mu(\mathbf{p}) \tag{312}$$

where of course we have only to retain the lowest-order contributions in γ and in C (γ^0, $C^{3/2}$). The $\mathbf{J}_0$ term is simply the current set up by the motion of independent ions (see Eq. (211)), while the correction term $\mathbf{J}_1$ is related to *both* the internal field effect and the electrophoretic effect discussed in Section V-A in a macroscopic way.

* Equation (309) shows that any extension of classical theory beyond the $C^{1/2}$ term is not consistent because, in classical theory, dissipation between ions is always neglected.

In order to compute these effects, we have to calculate explicitly Eq. (312) within the Brownian model specified by Eqs. (302) and (303).

In this section, we shall only discuss the relaxation term; however, before performing the detailed calculations corresponding to the precise Brownian model we have in mind, we shall first consider simpler cases, which already give a qualitatively correct description of the relaxation effect.

As already mentioned, the existence of a $C^{3/2}$ term in Eq. (312) is related to the long-range character of the Coulombic interactions between any pair of ions. We then have to take into account the collective interactions between many ions in the system; this in turn introduces a natural cut-off of the Coulomb force at a distance of the order κ^{-1}, where:

$$\kappa^2 = \frac{4\pi e^2}{\varepsilon k T} \sum_{\mu} Z_{\mu}^2 C_{\mu} \tag{313}$$

Of course, this result has to come out of the calculation and it will be obtained in Sections V-C and V-E. However, it is intuitively clear that a qualitatively correct result should come out of the "static approximation" using a screened coulomb potential (see

$$\bar{V}^{\mu\nu} = \frac{Z_{\mu} Z_{\nu} e^2}{\varepsilon r} \exp(-\kappa r) \tag{314}$$

the remark at the end of Section III). Moreover, we shall also provisionally neglect all interactions involving the solvent molecules:

$$V^{\mu 0} = V^{00} = 0 \tag{315}$$

except for the long-range part of these interactions which has been introduced in Eqs. (313) and (314) through the dielectric constant of the solvent, ε. We shall refer to this as the "plasma approximation" because, between two coulombic interactions, each ion moves freely, as in a completely ionized gas.

With these assumptions, it is readily verified that each term in (301) is finite, and we may thus restrict ourselves to the lowest-order term. Taking for $\rho_{\mathbf{k},-\mathbf{k}}^{(\alpha,\mu)}$ the Debye–Hückel result (168)

(which is of course consistent with Eq. (314)), we obtain from Eqs. (301), (16), and (97):

$$T_\alpha(\mathbf{p}_\alpha) = -\sum_\mu \frac{(4\pi e^2 Z_\alpha Z_\mu)^2}{8\pi^3 kT\varepsilon^2} C_\mu \int \frac{d\mathbf{k}}{(k^2+\kappa^2)^2} \int d\mathbf{p}_\mu \mathbf{k} \frac{\partial}{\partial \mathbf{p}_\alpha}$$
$$\times \frac{1}{\mathbf{k}(\mathbf{v}_\alpha - \mathbf{v}_\mu) - i0} \left[e\mathbf{E} Z_\alpha \frac{\partial}{\partial \mathbf{p}_\alpha} + e\mathbf{E} Z_\mu \frac{\partial}{\partial \mathbf{p}_\mu} \right] \phi_\alpha^{\text{eq.}} \phi_\mu^{\text{eq.}} \quad (316)$$

Inserting this expression into Eq. (312), the following expression for the current results:

$$\mathbf{J}_1^{p,s} = -\sum_{\mu,\nu} \frac{(4\pi e^2 Z_\nu Z_\mu)^2}{8\pi^3 \varepsilon^2 kT} \frac{e Z_\nu C_\mu C_\nu}{\zeta_\nu} \int \frac{d\mathbf{k}}{(k^2+\kappa^2)^2} \int d\mathbf{p}_\nu d\mathbf{p}_\mu$$
$$\times \mathbf{k} \frac{1}{[\mathbf{k}(\mathbf{v}_\nu - \mathbf{v}_\mu) - i0]} \left[e\mathbf{E} \frac{Z_\nu \mathbf{v}_\nu}{kT} + e\mathbf{E} \frac{Z_\mu \mathbf{v}_\mu}{kT} \right] \phi_\nu^{\text{eq.}} \phi_\mu^{\text{eq.}} \quad (317)$$

The integrals in Eq. (317) are readily performed; one first integrates over the momenta, taking into account that (here we take equal masses for simplicity):

$$\int d\mathbf{p}_\mu d\mathbf{p}_\nu \frac{v_{\mu z}}{v_{\mu z} - v_{\nu z}} \phi_\nu^{\text{eq.}} \phi_\mu^{\text{eq.}} = \frac{1}{2} \quad (318)$$

and the $\mathbf{k}$-integral is:

$$\int d\mathbf{k} \frac{\mathbf{k}(\mathbf{kE})}{k^2(k^2+\kappa^2)^2} = \frac{\pi^2}{3\kappa} \mathbf{E} \quad (319)$$

We thus obtain:

$$\mathbf{J}_1^{(p,s)} = -\frac{\pi \mathbf{E} e^6}{3\kappa(\varepsilon kT)^2} \sum_{\mu,\nu} \frac{C_\nu C_\mu}{\zeta_\nu} (Z_\nu^4 Z_\mu^2 - Z_\nu^3 Z_\mu^3) \quad (320)$$

$$\mathbf{J}_1^{(p,s)} = -\mathbf{J}_0 \frac{e^2 |Z_\alpha Z_\beta| \kappa}{12\varepsilon kT} \quad (321)$$

for a binary electrolyte with equal masses as desired. This is very similar to the classical result (297) and it will be discussed later (see Section V-F).

This simple result may be improved in various ways: first, we may relax the "static approximation" and keep the "plasma assumption" (315). In order to eliminate the divergences brought in by the long-range Coulomb interactions (114), it is then necessary to sum over an infinite class of diagrams, known as the "ring

contributions": this program was achieved by H. T. Davis and P. Résibois[5] and will be reported in Section V-C. Another improvement comes from a proper treatment of the interactions between the solvent and the ions: this is done in the next two sub-sections.[34]

C. The "Plasma-Dynamic Approximation"

As mentioned above, once the correct Coulomb interaction (114) is taken, the simple argument given in Section V-B is no longer correct because the lowest-order contribution (see Eq. (316)) diverges for small wave numbers. We have already encountered a similar problem in the equilibrium properties and it was resolved by summing the whole class of ring diagrams (see Fig. 9a). We shall now show that a similar method may be applied to analyze the relaxation effect; however, as we are now confronted with a dynamical problem, the explicit summation will be more complicated. It can however be performed making use of a factorization theorem proved by one of the authors.[29] The destruction operator $\langle 0|\tilde{\mathscr{D}}(0)|\{k\}\rangle$ in the ring approximation

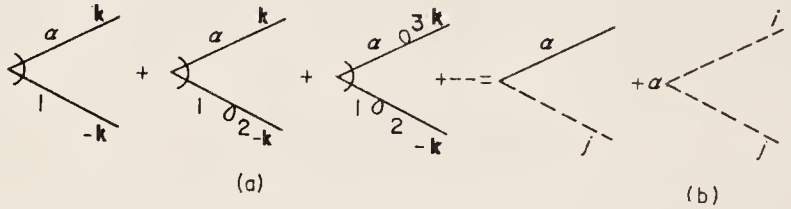

Fig. 11. Destruction operator in the ring approximation.

is given by the infinite class of diagrams illustrated in Fig. 11. These diagrams have two important characteristics:

(1) each particle only appears once, between two vertices, and then it transfers its total wave number k to another particle;

(2) taking aside the last vertex on the left, they describe interactions between two mutually independent groups of particles.

This latter property allows us to use the following *factorization theorem*: if in a dynamical process, two subgroups of particles are temporarily interacting independently of one another, then the time ordering between the interacting particles of one group is independent of the time ordering between the interacting particles of the other group.

In order to make the meaning of this theorem more precise, let us consider the Laplace inverse of $\langle 0|\tilde{\mathscr{D}}(z)|\mathbf{k}\rangle$, which is defined by a formula similar to (65):

$$\langle 0|\mathscr{D}(\tau)|\mathbf{k}\rangle = -\frac{1}{2\pi}\oint_C dz \exp(-iz\tau)\langle 0|\tilde{\mathscr{D}}(z)|\mathbf{k}\rangle \tag{322}$$

$$= \sum_{i=1}^{\infty}\left(\frac{\lambda}{i}\right)^n \int_0^\tau d\tau_1 \cdots \int_0^{\tau_{n-2}} d\tau_{n-1}\langle 0|\delta L(\tau)\delta L(\tau_1)\cdots\delta L(\tau_{n-1})|\mathbf{k}\rangle \tag{323}$$

with the definition:

$$\delta L(\tau) = \exp(iL_0\tau)\delta L \exp(-iL_0\tau) \tag{324}$$

Let us designate as an *F diagram* a contribution to Eq. (323) in which: (1) during the time from τ_i to τ_j the interactions can be separated into two subgroups, $\{r\}$ involving one set of particles, and $\{s\}$ involving the other set of different particles, and (2) all the interactions involving the group $\{r\}$ occur after the $\{s\}$ interactions (see Fig. 12a). Associated with this F diagram is a whole class, $\sum_F$, generated by taking all possible combinations of time orderings of numbers of the $\{s\}$ group with respect to the elements of the $\{r\}$ group, while maintaining the same time ordering within each group; an example is given in Fig. 12b.

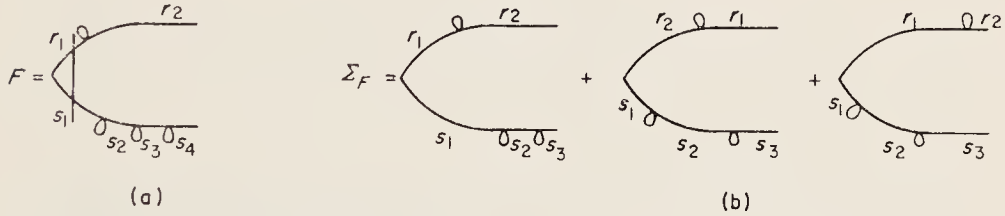

Fig. 12. An F diagram and its class Σ_F. (a) An F diagram. (b) The class Σ_F.

We can now state the theorem:
If,

$$F = \int_0^\tau d\tau_1 \cdots \int_0^{\tau_{i-1}} d\tau_i \int_0^{\tau_i} d\tau_{i+1} \cdots \int_0^{\tau_{i+l+m-1}} d\tau_{i+l+m} \int_0^{\tau_{i+l+m}} d\tau_j$$

$$\cdots \int_0^{\tau_{n-2}} d\tau_{n-1}\langle 0|\delta L(\tau)\cdots\delta L(\tau_i)\delta L^{r_1}(\tau_{i+1})\cdots\delta L^{r_l}(\tau_{i+l})$$

$$\delta L^{s_1}(\tau_{i+l+1})\cdots\delta L^{s_m}(\tau_{i+l+m})\delta L(\tau_i)\cdots\delta L(\tau_{n-1})|\mathbf{k}\rangle \tag{325}$$

then

$$\sum_F = \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \ldots \int_0^{\tau_{i-1}} d\tau_i \int_0^{\tau_i} d\tau_j \ldots \int_0^{\tau_{n-2}} d\tau_{n-1} \langle 0|\delta L(\tau) \ldots \delta L(\tau_i) G^{(r)}(\tau_i - \tau_j) G^{(s)}(\tau_i - \tau_j) \delta L(\tau_j) \ldots \delta L(\tau_{n-1})|\mathbf{k}\rangle \quad (326)$$

where

$$G^{(r)}(\tau) = \int_0^\tau d\tau_1 \ldots \int_0^{\tau_{l-1}} d\tau_l \delta L^{(r)}(\tau_1) \ldots \delta L^{(r)}(\tau_l) \quad (327)$$

which thus depends only on the $\{r\}$ group. $G^{(s)}(\tau)$ is defined similarly.

The physical meaning of this theorem is very intuitive and its proof will not be reported here (*loc. cit.*); it can easily be verified from the example of Fig. 12 and the general demonstration is obtained by induction.

Let us now rewrite the term $T_\alpha(\mathbf{p}_\alpha)$ of Eq. (301) within the ring approximation indicated in Fig. 11a. Using Eq. (106) for $w = 0$, we get:

$$T_\alpha^{(p,d)}(\mathbf{p}_\alpha) = -i \lim_{t\to\infty} \int_0^t d\tau \int d\mathbf{p}^{N-1} \{ \sum_k \sum_j \langle 0|\mathscr{D}_{\alpha j}^{\text{Ring}}(\tau)|\mathbf{k}, -\mathbf{k}\rangle \times L^E \rho_{\mathbf{k},-\mathbf{k}}^{(\alpha j)\text{eq.}} + \sum_k \sum_{ij} \langle 0|\mathscr{D}_{\alpha ij}^{\text{Ring}}(\tau)|\mathbf{k}, -\mathbf{k}\rangle L^E \rho_{\mathbf{k},-\mathbf{k}}^{(ij)\text{eq.}} \} \quad (328)$$

where we have separated the diagrams of Fig. 11 into a sum of terms in which the reference particles α does not interact during the time interval $(0, \tau)$ and another sum in which α interacts at least once during that time interval; this separation is schematically indicated in Fig. 11b.

Also, the notation (p, d) means "plasma, dynamic" and for $\rho_{\mathbf{k},-\mathbf{k}}^{(ij)\text{eq.}}$, we have of course to take the equilibrium distribution (168).

Now, the electric field operator L^E, appearing in Eq. (328), has been defined as

$$L^E = \sum_n \frac{eZ_n}{i} \mathbf{E} \cdot \frac{\partial}{\partial \mathbf{p}_n}$$

but it is clear from Eq. (328) that for each destruction diagram, only a limited number of terms in L^E will survive; indeed, all terms go to zero by integration except those for which the index n

is the same as for one of the particles which appears in the destruction diagram.

For instance, considering:

$$Z_n \frac{e}{i} \mathbf{E} \frac{\partial}{\partial \mathbf{p}_n} \rho^{(ij)\text{eq.}}_{\mathbf{k},-\mathbf{k}} \tag{329}$$

we get zero if n is different from α, i, and j because

$$\int d\mathbf{p}_n \frac{\partial}{\partial \mathbf{p}_n} \phi_n^{\text{eq.}} = 0$$

Consequently, we may further decompose Eq. (328) into:

$$T_\alpha^{(\text{p,d})}(\mathbf{p}_\alpha) = T_\alpha^{\text{I}} + T_\alpha^{\text{II}} + T_\alpha^{\text{III}} + T_\alpha^{\text{IV}} + T_\alpha^{\text{V}} \tag{330}$$

where (see Eq. (158)):

$$T_\alpha^{\text{I}} = -\lim_{t\to\infty} \int_0^t d\tau \int dp^{N-1} \sum_k \sum_j \langle 0 | \mathscr{D}_{\alpha j}^{\text{Ring}}(\tau) | \mathbf{k}, -\mathbf{k} \rangle \times e\mathbf{E} \left(Z_\alpha \frac{\partial}{\partial \mathbf{p}_\alpha} + Z_j \frac{\partial}{\partial \mathbf{p}_j} \right) Z_\alpha Z_j g_k \prod_l \phi_l^{\text{eq.}} \tag{331}$$

$$T_\alpha^{\text{II}} = -\lim_{t\to\infty} \int_0^t d\tau \int dp^{N-1} \sum_k \sum_{jn} \langle 0 | \mathscr{D}_{\alpha jn}^{\text{Ring}}(\tau) | \mathbf{k}, -\mathbf{k} \rangle \times e\mathbf{E} Z_n \frac{\partial}{\partial \mathbf{p}_n} Z_\alpha Z_j g_k \prod_l \phi_l^{\text{eq.}} \tag{332}$$

which denotes the case where the accelerated n particle appears again in the destruction term;

$$T_\alpha^{\text{III}} = -\lim_{t\to\infty} \int_0^t d\tau \int dp^{N-1} \sum_k \sum_{ij} \langle 0 | \mathscr{D}_{\alpha ij}^{\text{Ring}}(\tau) | \mathbf{k}, -\mathbf{k} \rangle \times e\mathbf{E} \left(Z_i \frac{\partial}{\partial \mathbf{p}_i} + Z_j \frac{\partial}{\partial \mathbf{p}_j} \right) Z_i Z_j g_k \prod_l \phi_l^{\text{eq.}} \tag{333}$$

$$T_\alpha^{\text{IV}} = -\lim_{t\to\infty} \int_0^t d\tau \int dp^{N-1} \sum_k \sum_{ijn} \langle 0 | \mathscr{D}_{\alpha ijn}^{\text{Ring}}(\tau) | \mathbf{k}, -\mathbf{k} \rangle \times e\mathbf{E} Z_n \frac{\partial}{\partial \mathbf{p}_n} Z_i Z_j g_k \prod_l \phi^{l\text{eq.}} \tag{334}$$

and finally:*

$$T_\alpha^{\mathrm{V}} = -\lim_{t\to\infty}\int_0^t d\tau \int dp^{N-1} \sum_k \sum_{ij} \langle 0|\mathscr{D}_{\alpha ij}^{\mathrm{Ring}}(\tau)|\mathbf{k}, -\mathbf{k}\rangle \times e\mathbf{E}\cdot Z_\alpha \frac{\partial}{\partial \mathbf{p}_\alpha} Z_i Z_j g_k \prod_l \phi_l^{\mathrm{eq.}} \qquad (335)$$

These five terms, which will now be explicitly evaluated, are schematically represented in Fig. 13.

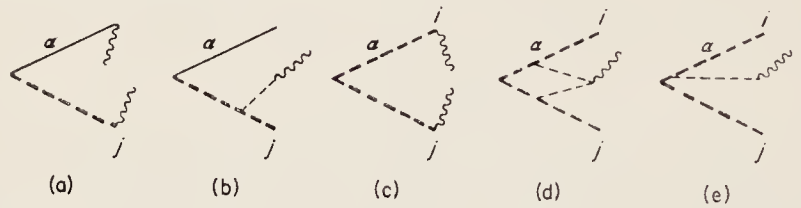

Fig. 13. The five contributions (330) to $T_\alpha(\mathbf{p}_\alpha)$. (a) T_α^{I}; (b) T_α^{II}; (c) T_α^{III}; (d) T_α^{IV}; (e) T_α^{V}.

We are now ready to apply the factorization theorem. Starting with Eq. (331) and making the various matrix elements explicit, we obtain:

$$T_\alpha^{\mathrm{I}} = i\sum_k \sum_j \int_0^\infty d\tau \int d\mathbf{p}_j \Omega^{-1}\mathbf{k} V_k \frac{\partial}{\partial \mathbf{p}_\alpha}[Z_\alpha \exp(-i\mathbf{k}\mathbf{v}_\alpha\tau)] \times [Z_j G^{(j)}(-\mathbf{k}, \tau)] e\mathbf{E}\left(Z_\alpha \frac{\partial}{\partial \mathbf{p}_\alpha} + Z_j \frac{\partial}{\partial \mathbf{p}_j}\right) Z_\alpha Z_j g_k \phi_\alpha^{\mathrm{eq.}} \phi_j^{\mathrm{eq.}} \qquad (336)$$

where we have set:

$$V_k = 4\pi e^2/\varepsilon k^2 \qquad (337)$$

and:

$$G^{(j)}(\mathbf{k}, \tau) = \exp(i\mathbf{k}\mathbf{v}_j\tau) - i\left\{\sum_n \int d\mathbf{p}_n \int_0^\tau d\tau_1 \exp[i\mathbf{k}\mathbf{v}_n(\tau - \tau_1)]\Omega^{-1} \times Z_n^2 \mathbf{k} V_k \frac{\partial \phi_n^{\mathrm{eq.}}}{\partial \mathbf{p}_n} \exp(i\mathbf{k}\mathbf{v}_j\tau_1)\right\} + (-i^2)\sum_n \sum_m \int d\mathbf{p}_n \int d\mathbf{p}_m \int_0^\tau d\tau_1 \int_0^{\tau_1} d\tau_2 \times \exp[i\mathbf{k}\mathbf{v}_m(\tau - \tau_1)]\Omega^{-1} Z_m^2 \mathbf{k} V_k \frac{\partial \phi_m^{\mathrm{eq.}}}{\partial p_m} \times \exp[i\mathbf{k}\mathbf{v}_n(\tau_1 - \tau_2)]\Omega^{-1} Z_n^2 \mathbf{k} V_k \frac{\partial \phi_n^{\mathrm{eq.}}}{\partial \mathbf{p}_n} \exp(i\mathbf{k}\mathbf{v}_j\tau_2) + \ldots \qquad (338)$$

* This term was overlooked in the original Davis–Résibois paper.

Using the convolution theorem for Laplace transforms, we rewrite Eq. (336) as:

$$T_\alpha^{\mathrm{I}} = \frac{i}{\Omega}\sum_{\mathbf{k}}\sum_{j}\int_0^\infty d\tau\int d\mathbf{p}_j \mathbf{k}V_k\frac{\partial}{\partial \mathbf{p}_\alpha}\left\{-\frac{1}{2\pi i}\oint_C dz\exp(-iz\tau)Z_\alpha Z_j \right.$$
$$\left.\times \tilde{G}^{(j)}(-\mathbf{k}; z-\mathbf{k}\mathbf{v}_\alpha)e\mathbf{E}\left(Z_\alpha\frac{\partial}{\partial \mathbf{p}_\alpha}+Z_j\frac{\partial}{\partial \mathbf{p}_j}\right)Z_\alpha Z_j g_k\phi_\alpha^{\mathrm{eq.}}\phi_j^{\mathrm{eq.}}\right. \quad (339)$$

where:

$$\tilde{G}^{(j)}(\mathbf{k}; z) = \frac{1}{\mathbf{k}\mathbf{v}_j - z}[1+\sum_n Z_n^2\Omega^{-1}J_n^+(\mathbf{k}; z)+\sum_n\sum_m Z_n^2Z_m^2$$
$$\times\Omega^{-2}J_n^+(\mathbf{k}; z)J_m^+(\mathbf{k}; z)+\ldots] \quad (340)$$

In this last formula, we have used the definition:

$$J_n^+(\mathbf{k}; z) = \int d\mathbf{p}_n(\mathbf{k}\mathbf{v}_n - z)^{-1}\mathbf{k}V_k\frac{\partial\phi_n^{\mathrm{eq.}}}{\partial \mathbf{p}_n} \quad (341)$$

The summation over the dummy variables n, m. . . can be performed explicitly and, setting

$$J^+(\mathbf{k}; z) = \sum_{\mu=\alpha,\beta} Z_\mu^2 C_\mu J_\mu^+(\mathbf{k}; z) \quad (342)$$

we get the simple result:

$$T_\alpha^{\mathrm{I}} = \frac{iZ_\alpha^2}{8\pi^3}\sum_j\int d\mathbf{k}\int d\mathbf{p}_j\int_0^\infty d\tau\mathbf{k}V_k\frac{\partial}{\partial \mathbf{p}_\alpha}\left\{-\frac{1}{2\pi i}\oint_C dz\exp(-iz\tau)\right.$$
$$\times[1-J^+(-\mathbf{k}; z-\mathbf{k}\mathbf{v}_\alpha)]^{-1}Z_j^2[\mathbf{k}\mathbf{v}_{\alpha j}-z]^{-1}$$
$$\left.\times e\mathbf{E}\left(Z_\alpha\frac{\partial}{\partial \mathbf{p}_\alpha}+Z_j\frac{\partial}{\partial \mathbf{p}_j}\right)g_k\phi_\alpha^{\mathrm{eq.}}\phi_j^{\mathrm{eq.}}\right\} \quad (343)$$

If we insert Eq. (170) for g_k and perform the τ integration (see Eq. (73) for a similar case) as well as the summation over j, we get:

$$T_\alpha^{\mathrm{I}} = -\frac{4\pi Z_\alpha^2\beta}{(8\pi^3)\varepsilon}\int\frac{d\mathbf{k}}{(k^2+\kappa^2)}\mathbf{k}V_k\frac{\partial}{\partial \mathbf{p}_\alpha}\left\{\lim_{t\to\infty}\frac{1}{2\pi i}\oint\frac{\exp(-izt)}{z}dz\right.$$
$$\times[1-J^+(-\mathbf{k}; z-\mathbf{k}\mathbf{v}_\alpha)]^{-1}[P'(-\mathbf{k}; z-\mathbf{k}\mathbf{v}_\alpha)]Z_\alpha$$
$$\left.\times e\mathbf{E}\frac{\partial\phi_\alpha^{\mathrm{eq.}}}{\partial \mathbf{p}_\alpha}+\mathbf{E}\mathbf{J}'(-\mathbf{k}; z-\mathbf{k}\mathbf{v}_\alpha)\phi_\alpha^{\mathrm{eq.}}]\right\} \quad (344)$$

where

$$\mathbf{J}'(\mathbf{k};z) = \sum_{\mu} e^3 Z_\mu^3 C_\mu \int d\mathbf{p}_\mu \frac{1}{\mathbf{k}\mathbf{v}_\mu - z} \frac{\partial}{\partial \mathbf{p}_\mu} \phi_\mu^{\text{eq.}} \tag{345}$$

$$P'(\mathbf{k};z) = \sum_{\mu} e^2 Z_\mu^2 C_\mu \int d\mathbf{p}_\mu \frac{1}{\mathbf{k}\mathbf{v}_\mu - z} \phi_\mu^{\text{eq.}} \tag{346}$$

In order to evaluate the contour integral, we note that the functions J^+, P', and $\mathbf{J}'$ are of the Cauchy type (see Section II-D); the only contribution in the limit $t \to \infty$ therefore comes from the pole at $z = 0$, with the result:

$$T_\alpha^{\text{I}} = -\frac{(4\pi)^2 e^2 Z_\alpha^2 \beta}{8\pi^3 \varepsilon^2} \int \frac{d\mathbf{k}}{(k^2 + \kappa^2)} \frac{\mathbf{k}}{k^2} \frac{\partial}{\partial \mathbf{p}_\alpha} [1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)]^{-1}$$
$$\left[P'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha) Z_\alpha e \mathbf{E} \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial \mathbf{p}_\alpha} + \mathbf{E}\mathbf{J}'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha) \phi_\alpha^{\text{eq.}} \right] \tag{347}$$

We shall postpone the discussion of the $\mathbf{k}$ integration and consider the other terms $T_\alpha^i (i > 1)$. The contribution represented by Eq. (332) can be handled in the same fashion as Eq. (331); the final expression is:

$$T_\alpha^{\text{II}} = -\frac{(4\pi)^2 e^2 Z_\alpha^2 \beta}{(8\pi^3) \varepsilon^2} \int \frac{d\mathbf{k}}{(k^2 + \kappa^2)} \frac{\mathbf{k}}{k^2} \frac{\partial}{\partial \mathbf{p}_\alpha} [1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)]^{-2}$$
$$\times \mathbf{E}\mathbf{G}(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha) P'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha) \phi_\alpha^{\text{eq.}} \tag{348}$$

with the new function:

$$\mathbf{G}(\mathbf{k};z) = \sum_{\mu} e Z_\mu^3 C_\mu \int d\mathbf{p}_\mu \frac{1}{(\mathbf{k}\mathbf{v}_\mu - z)} \left(\mathbf{k} V_k \frac{\partial}{\partial \mathbf{p}_\mu} \right) \frac{\partial}{\partial \mathbf{p}_\mu} \phi_\mu^{\text{eq.}} \tag{349}$$

Turning to Eq. (333) and applying the factorization theorem for this class of terms, we find:

$$T_\alpha^{\text{III}} = i \sum_k \sum_{i,j} \int_0^\infty d\tau \int d\mathbf{p}_i d\mathbf{p}_j \Omega^{-1} \mathbf{k} V_k \frac{\partial}{\partial \mathbf{p}_\alpha} [Z_\alpha^2 Z_i^2 G^{(\alpha i)}(\mathbf{k};\tau)]$$
$$\times [Z_j G^{(j)}(-\mathbf{k};\tau)] e\mathbf{E} \left(Z_i \frac{\partial}{\partial \mathbf{p}_i} + Z_j \frac{\partial}{\partial \mathbf{p}_j} \right) Z_i Z_j g_k \phi_i^{\text{eq.}} \phi_j^{\text{eq.}} \tag{350}$$

where the new quantity:

$$G^{(\alpha i)}(\mathbf{k},\tau) = i\left\{\int_0^\tau d\tau_1 \exp\left[-i\mathbf{k}\mathbf{v}_\alpha(\tau-\tau_1)\right]\Omega^{-1}\mathbf{k}\cdot V_k \frac{\partial\phi_\alpha^{\text{eq.}}}{\partial\mathbf{p}_\alpha}\exp\left(-i\mathbf{k}\mathbf{v}_i\tau_1\right)\right\}$$
$$+ |i^2|\left\{\sum_{\mathbf{n}}\int_0^\tau\int_0^{\tau_1} d\tau_1 d\tau_2 \exp\left[-i\mathbf{k}\mathbf{v}_\alpha(\tau-\tau_1)\right]\Omega^{-1}Z_\alpha^2\mathbf{k}V_k \frac{\partial\phi_\alpha^{\text{eq.}}}{\partial\mathbf{p}_\alpha}\right.$$
$$\left.\times \exp\left[-i\mathbf{k}\mathbf{v}_n(\tau_1-\tau_2)\right]\Omega^{-1}Z_n^2\mathbf{k}V_k \frac{\partial\phi_n^{\text{eq.}}}{\partial\mathbf{p}_n}\exp\left(-i\mathbf{k}\mathbf{v}_i\tau_2\right)\right\} + \ldots \tag{351}$$

has been introduced.

The Laplace transform of Eq. (351) reduces to the simple product:

$$\tilde{G}^{(\alpha i)}(\mathbf{k};z) = \Omega^{-1}\frac{1}{\mathbf{k}\mathbf{v}_\alpha - z}\mathbf{k}V_k\frac{\partial\phi_\alpha^{\text{eq.}}}{\partial\mathbf{p}_\alpha}\left[1-J^+(\mathbf{k};z)\right]^{-1}\frac{1}{\mathbf{k}\mathbf{v}_i - z} \tag{352}$$

and we thus get for T_α^{III}:

$$T_\alpha^{\text{III}} = \frac{i}{\Omega}\sum_{\mathbf{k}}\sum_{i,j}\int_0^\infty d\tau\int d\mathbf{p}_i\int d\mathbf{p}_j\mathbf{k}V_k\frac{\partial}{\partial\mathbf{p}_\alpha}\left\{\left(-\frac{1}{2\pi i}\right)^2\oint_{C_1}dz_1\oint_{C_2}dz_2\right.$$
$$\left.\times\exp\left[-i(z_1+z_2)\tau\right]\right\}\left[Z_\alpha^2Z_i\tilde{G}^{(\alpha i)}(\mathbf{k};z_1)\right]\left[Z_j\tilde{G}^{(j)}(-\mathbf{k};z_2)\right]$$
$$\times e\mathbf{E}\cdot\left(Z_i\frac{\partial}{\partial\mathbf{p}_i}+Z_j\frac{\partial}{\partial\mathbf{p}_j}\right)Z_iZ_jg_k\phi_i^{\text{eq.}}\phi_j^{\text{eq.}} \tag{353}$$

By elementary transformations, similar to the ones leading to Eq. (344), we then get:

$$T_\alpha^{\text{III}} = -\frac{1}{\Omega^2}\sum_{i,j}\frac{4\pi e^2\beta Z_\alpha^2Z_i^2Z_j^2}{8\pi^3\varepsilon}\int\frac{d\mathbf{k}}{(k^2+\kappa^2)}\int d\mathbf{p}_i\int d\mathbf{p}_j\mathbf{k}V_k\frac{\partial}{\partial\mathbf{p}_\alpha}$$
$$\times\left\{-\lim_{\tau\to\infty}\left(-\frac{1}{2\pi i}\right)^2\oint_{C_1}\oint_{C_2}dz_1dz_2\frac{\exp\left[-i(z_1+z_2)\tau\right]}{(z_1+z_2)}\right.$$
$$\times\left[\frac{1}{\mathbf{k}\mathbf{v}_\alpha - z_1}\mathbf{k}V_k\frac{\partial\phi_\alpha^{\text{eq.}}}{\partial\mathbf{p}_\alpha}\left[1-J^+(\mathbf{k};z_1)\right]^{-1}\frac{1}{\mathbf{k}\mathbf{v}_i - z_1}\right]$$
$$\times\left[\left[1-J^+(-\mathbf{k};z_2)\right]^{-1}\frac{1}{(-\mathbf{k}\mathbf{v}_j - z_2)}\right]$$
$$\left.\times e\mathbf{E}\cdot\left(Z_i\frac{\partial}{\partial\mathbf{p}_i}+Z_j\frac{\partial}{\partial\mathbf{p}_j}\right)\phi_i^{\text{eq.}}\phi_j^{\text{eq.}}\right\} \tag{354}$$

$$= -\frac{(4\pi)^3 e^2 Z_\alpha^2 \beta}{8\pi^3 \varepsilon^3} \int \frac{d\mathbf{k}}{(k^2+\kappa^2)} \frac{\mathbf{k}}{k^2} \frac{\partial}{\partial \mathbf{p}_\alpha} \left\{ -\lim_{\tau\to\infty} \left(-\frac{1}{2\pi i} \right)^2 \oint_{C_1} \oint_{C_2} dz_1 dz_2 \right.$$
$$\times \frac{\exp[-i(z_1+z_2)\tau]}{(z_1+z_2)} \left[\frac{1}{(\mathbf{k}\mathbf{v}_\alpha - z_1)} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial \mathbf{p}_\alpha} [1 - J^+(\mathbf{k}; z_1)]^{-1} \right]$$
$$\times [1 - J^+(-\mathbf{k}; z_2)]^{-1} [\mathbf{E}\cdot\mathbf{J}'(\mathbf{k}; z_1) P'(-\mathbf{k}; z_2)$$
$$\left. + \mathbf{E}\cdot\mathbf{J}'(-\mathbf{k}; z_2) P'(\mathbf{k}; z_1)] \right\} \tag{355}$$

The contour integration over z_1 and z_2 is rather delicate. The simplest method is first to express the integral in Eq. (355) as a sum of its two halves and then in one of the halves to make the transformation $\mathbf{k} \to -\mathbf{k}$; $z_1 \to z_2$; $z_2 \to z_1$. This change of variables only affects the term $(\mathbf{k}\mathbf{v}_\alpha - z_1)^{-1}$ since everything else is symmetrical to the transformation. Therefore, instead of $(\mathbf{k}\mathbf{v}_\alpha - z_1)^{-1}$, we get in Eq. (355):

$$\frac{1}{2} \left[\frac{1}{\mathbf{k}\mathbf{v}_\alpha - z_1} - \frac{1}{\mathbf{k}\mathbf{v}_\alpha + z_2} \right] = \frac{1}{2} \frac{(z_1+z_2)}{(\mathbf{k}\mathbf{v}_\alpha - z_1)(\mathbf{k}\mathbf{v}_\alpha + z_2)} \tag{356}$$

The factor $(z_1 + z_2)$ in the numerator cancels the one in the denominator and therefore the two integrations can be performed separately. Their evaluation follows exactly the argument given in obtaining Eq. (347); the result is

$$T_\alpha^{\text{III}} = -\frac{(4\pi)^3 e^2 Z_\alpha^2 \beta}{8\pi^3 \varepsilon^3} \int \frac{d\mathbf{k}}{(k^2+\kappa^2)} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial}{\partial \mathbf{p}_\alpha} \left\{ \frac{1}{2} e\mathbf{E} \cdot \right.$$
$$\left. \frac{\mathbf{J}'(\mathbf{k}: \mathbf{k}\mathbf{v}_\alpha) P'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha) + \mathbf{J}'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha) P'(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha)}{[1 - J^+(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha)][1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)]} \right\} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial \mathbf{p}_\alpha}$$

Since nothing new is introduced in evaluating the last two terms, Eqs. (334), (335), we merely quote the final expressions, which are:

$$T_\alpha^{\text{IV}} = -\frac{(4\pi)^3 e^2 Z_\alpha^2 \beta}{8\pi^3 \varepsilon^3} \int \frac{d\mathbf{k}}{(k^2+\kappa^2)} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial}{\partial \mathbf{p}_\alpha}$$
$$\times \left\{ \frac{1}{2} \frac{P'(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha) P'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)}{[1 - J^+(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha)][1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha]} \right.$$
$$\left. \times \mathbf{E} \cdot \left[\frac{\mathbf{G}(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha)}{[1 - J^+(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha)]} - \frac{\mathbf{G}(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)}{[1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)]} \right] \right\} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial \mathbf{p}_\alpha} \tag{358}$$

and:

$$T_\alpha^{\mathrm{V}} = -\frac{(4\pi)^3 e^2 Z_\alpha^2 \beta}{8\pi^3 \varepsilon^3} \int \frac{d\mathbf{k}}{(k^2+\kappa^2)} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial}{\partial \mathbf{p}_\alpha} \times \frac{1}{2} \frac{P'(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha) P'(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)}{[1 - J^+(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha)][1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)]} \frac{\mathbf{k}}{k^2} \cdot \frac{\partial}{\partial \mathbf{p}_\alpha} \mathfrak{E} e Z_\alpha \cdot \frac{\partial \phi_\alpha^{\mathrm{eq.}}}{\partial \mathbf{p}_\alpha} \tag{359}$$

The remainder of the calculation is now very simple *in principle*: Eqs. (347), (348), (357), (358), and (359) are inserted into Eq. (312) and the remaining integrals over $\mathbf{k}$ and $\mathbf{v}_\alpha$ are evaluated.

However, the calculations are tedious and we shall not report them here: in the final stage, we are left with a complicated one-variable integral involving in the integrand various combinations of error functions which are well known in plasma theory.[10] One has then to evaluate this last integral by some numerical procedure.

Instead of giving the details of these calculations, we shall merely exemplify it by an example in Appendix 1 and we limit ourselves here to a general discussion of the conclusions.

(1) As is readily verified, *each of the integrals defining respectively* T_α^{I}, T_α^{II}, T_α^{III}, T_α^{IV}, *and* T_α^{V} *does not diverge for small wave numbers*: as was expected, the summation of the ring contributions has entirely suppressed the short wavelength divergence of the original series, by introducing a natural cut-off at the inverse Debye length κ.

(2) As is readily verified by dimensional analysis each contribution makes a contribution to the current:

$$\mathbf{J}_1^{(p,d)} \sim \mathbf{J}_0 \frac{e^2 \kappa}{\varepsilon k T} \tag{360}$$

In other words, our detailed calculation confirms the qualitative description which was given by Eq. (321) in the "plasma static" approximation.

Moreover, preliminary numerical calculation confirms that one may even write:

$$\mathbf{J}_1^{(p,d)} = -\mathbf{J}_0 \frac{e^2 \kappa |Z_\alpha Z_\beta|}{12 \varepsilon k T} \gamma\left(\frac{m_\alpha}{m_\beta}; \frac{Z_\alpha}{Z_\beta}\right) \tag{361}$$

where γ is a positive dimensionless constant, depending in a complicated manner on the ratio of the masses and of the charges

of the ions, which for a reasonable electrolyte is not far from unity ($\gamma(1,1) \simeq 0.9$). However, we do not want to discuss here the possible implications of this mass dependence because the model used is, of course, still very crude.

We prefer to turn now to a more precise description of the interactions between the ions and the solvent; this is done in the following two sections.

D. The "Brownian-Static" Approximation

In the previous section, we verified that the screened Debye potential (314) does indeed give a satisfactory approximation for the collective interaction in the conductance of electrolytes. However, we have not yet considered the effect of the interactions with the solvent.

In this section, we want to get rid of condition (315) and we want to investigate the effect of a short-range interaction between ion–solvent and solvent–solvent molecules; we thus have

$$V^{\mu,0},\ V^{0,0} \neq 0 \tag{362}$$

We shall, however, keep here the screened Coulomb potential (314) for describing the interionic interaction; the most general case will be discussed in Section V-E.

This problem is very difficult to solve in general; however, we have to keep conditions (303) in mind, which we used in order to obtain the Fokker–Planck collision term (304). With this approximation, it is expected that the ions will exhibit random Brownian motion instead of free particle motion between two successive coulombic interactions. We shall thus refer to this model as the "Brownian-static" model (B.s.).

If we take the interactions of the solvent into account, new possibilities are offered in the possible diagrams for the destruction term; to the lowest orders in the screened potential (314), we have new diagrams of the type illustrated in Fig. 14.

In Fig. 14a we have indicated a typical diagram where we have *no* Coulombic interaction between the two ions α and β; instead of this, solvent molecule j—which is represented by a dotted line—exactly transfers the total wave number $\mathbf{k}$ from particle β to particle α. This diagram will thus not give a contribution of

order e^6 to the current, as the simple case of Eq. (320), but rather a contribution of order e^4. It is thus in another category of terms and we shall not discuss it here because it does not play a role in the relaxation effect. We do not mean of course that this diagram is negligible; however it describes a different physical effect. More precisely, we shall show in the next section that this graph

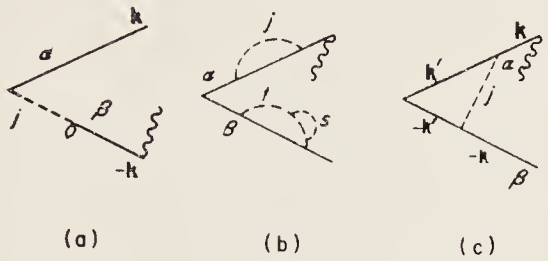

Fig. 14. A few diagrams involving solvent–ion and solvent–solvent interactions.

is the simplest of a whole class that generates the well-known *electrophoretic effect.*

On the contrary, Figs. 14b and 14c both give a contribution of the order e^6 to the current; they have however a completely different behavior in the limit of small wave numbers. Indeed in Fig. 14b, no solvent molecule interacts with both ions; as we shall see below, this diagram gives a contribution to the limiting law and has to be retained. On the other hand, Fig. 14c shows a process in which molecule j interacts with both ions α and β. Due to the short-range of the forces $V^{\mu,0}$, this kind of term may be neglected, as we now show; we have (Latin indices refer to solvent molecules):

$$T_\alpha^{(4,4c)} = \sum_{k,k'} N_\beta N_j \int d\mathbf{v}_j \int d\mathbf{v}_\beta \mathbf{k}' \frac{4\pi e^2 Z_\alpha Z_\beta}{\varepsilon(k'^2 + \kappa^2)} \frac{\partial}{\partial \mathbf{p}_\alpha}$$
$$\times \frac{1}{\mathbf{k}'\mathbf{v}_{\alpha\beta} - i0} (\mathbf{k} - \mathbf{k}') V^{\beta,0}_{|\mathbf{k}-\mathbf{k}'|} \frac{\partial}{\partial \mathbf{p}_\beta} \frac{1}{\mathbf{k}'\mathbf{v}_\alpha + (\mathbf{k} - \mathbf{k}')\mathbf{v}_j - \mathbf{k}\mathbf{v}_\beta - i0}$$
$$\times (\mathbf{k} - \mathbf{k}') V^{\alpha 0}_{|\mathbf{k}-\mathbf{k}'|} \left(\frac{\partial}{\partial \mathbf{p}_\alpha} - \frac{\partial}{\partial \mathbf{p}_j} \right) \frac{1}{\mathbf{k}\mathbf{v}_{\alpha\beta} - i0} \frac{e\mathbf{E}}{i} Z_\alpha \frac{\partial}{\partial \mathbf{p}_\alpha}$$
$$\times \left(- \frac{4\pi e^2 Z_\alpha Z_\beta}{\varepsilon k T (k^2 + \kappa^2)} \right) \phi_\alpha^{\text{eq.}} \phi_\beta^{\text{eq.}} \phi_j^{\text{eq.}} \tag{363}$$

The behavior of this integral for small wave numbers is readily obtained by taking $V_{\mathbf{k}}^{\mu,0} \approx$ constant. By dimensional arguments, we then find, dropping all unimportant constants:

$$T_{\alpha}^{(4.4c)} \sim C_{\beta} \int d\mathbf{k} \int d\mathbf{k}' \frac{k^2 k'^2}{(k^2 + \kappa^2)(k'^2 + \kappa^2)} \sim C_{\beta}\kappa^2 \sim C_{\beta}C_{\nu} \quad (364)$$

which is negligible in the limit of a dilute electrolyte.

The analysis given here on these simple examples is readily extended to more complicated situations; the conclusion is that, precisely as for the ring diagrams of Coulombic interactions, the only diagrams which have to be retained are of the general type indicated in Fig. 15, where each ion interacts independently with different solvent molecules: in each intermediate state where the ions are non-interacting, the wave number is conserved and equal to $\mathbf{k}$ or $-\mathbf{k}$. Moreover, another important feature of these graphs is that they are all of the "$\sum_F$ type" defined in Eq. (326), for which the factorization theorem holds.

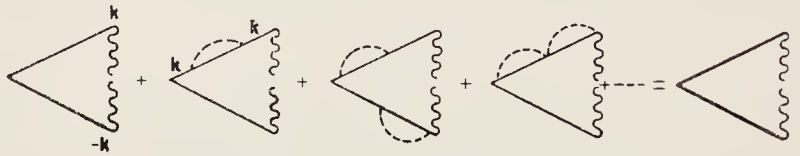

Fig. 15. Relevant diagrams.

The summation of the series given in Fig. 15 runs exactly along the lines followed for the "plasma-dynamic" case treated in Section V-C. We shall thus merely quote the final result; the sum of the graphs of Fig. 15 may be written as:

$$T_{\alpha}^{(15)} = -\lim_{t\to\infty} \int_0^t d\tau \sum_{\mu} N_{\mu} \int d\mathbf{p}_{\mu} \sum_{k} \langle 0|\delta L^{\alpha\mu}|\mathbf{k}, -\mathbf{k}\rangle \times G^{\alpha}(\mathbf{k}, \tau) G^{\mu}(-\mathbf{k}; \tau) L^{E} \rho_{\mathbf{k},-\mathbf{k}}^{(\alpha,\mu)\text{eq.}} \quad (365)$$

where $G^{\alpha}(\mathbf{k}, \tau)$ describes the propagation of ion α in the fluid and is given by:

$$G^{\alpha}(\mathbf{k}; \tau) = -\frac{1}{2\pi i} \oint_C dz \exp(-iz\tau) \tilde{G}^{\alpha}(\mathbf{k}; z) \quad (366)$$

$$\tilde{G}^{\alpha}(\mathbf{k}; z) = \int \prod_{i=1}^{N_0} d\mathbf{p}_i \langle \mathbf{k}_{\alpha}; \{0\} \left| \frac{1}{L^{\alpha} - z} \right| \mathbf{k}_{\alpha}; \{0\} \rangle \prod_{i=1}^{N_0} \phi_i^{\text{eq.}} \quad (367)$$

Here L^α is the Liouville operator of ion α plus the fluid; it corresponds to the Hamiltonian:

$$H^\alpha = H_0^\alpha + \lambda V^\alpha \tag{368}$$

$$H_0^\alpha = \frac{p_\alpha^2}{2m_\alpha} + \sum_{i=1}^{N_0} \frac{p_i^2}{2m_0} \tag{369}$$

$$\lambda V^\alpha = \sum_{i=1}^{N_0} V^{\alpha 0}(|\mathbf{r}_\alpha - \mathbf{r}_i|) + \sum_{i>j} V^{00}(|\mathbf{r}_i - \mathbf{r}_j|) \tag{370}$$

A similar problem was discussed in Section IV-C, where the motion of a single ion in the solvent was considered. We shall briefly indicate in Appendix A2 how this calculation may be generalized to the case where the heavy particle has a non-vanishing wave number. The resolvant operator is decomposed into irreducible diagonal fragments, which are then expanded in powers of γ_α; the result is:

$$\tilde{G}^\alpha(\mathbf{k}; z) = \frac{1}{\mathbf{k}\mathbf{v}_\alpha - \square_{\mathbf{k}}^\alpha(z) - z} \tag{371}$$

where

$$\square_{\mathbf{k}}^\alpha(z) = \gamma_\alpha \square_{\mathbf{k}}^{\alpha(1)}(z) + \gamma_\alpha^2 \square_{\mathbf{k}}^{\alpha(2)}(z) + O(\gamma_\alpha^3) \tag{372}$$

As the explicit form of these operators is not needed here, we shall refer the reader to Appendix A2 for the definition of these quantities.

It may appear surprising at first sight that we should keep explicitly γ_α^2 terms in Eq. (372) because in Eq. (371) the average velocity $\langle \mathbf{v}_\alpha \rangle$ is of order γ_α and thus seems to be dominant in a first approximation. However, we should keep in mind that we are interested in values of $\mathbf{k}$ which are very small, of the order of the inverse Debye length κ. In the limit of infinite dilution, we may reach a regime where

$$\kappa C^{-1/3} \leq \gamma_\alpha \tag{373}$$

in which case we have to keep the γ_α^2 contribution in Eq. (372)! More precisely, for values of $\mathbf{k}$ which are of the order κ, we have:

$$\langle \mathbf{k}\mathbf{v}_\alpha \rangle \sim \gamma_\alpha \kappa \sqrt{(kT/m_0)} \tag{374}$$

while we may forecast from Eq. (304) that:

$$\square_{\mathbf{k}}^{\alpha(2)} \sim \gamma_\alpha^2 \zeta_\alpha / m_0 \tag{375}$$

Two cases are then possible: (1) we may first have:

$$\zeta_\alpha^2/m_\alpha \ll e^2C/\varepsilon \tag{376}$$

which we shall refer to as the "small friction" case. Then, the $\square_{\mathbf{k}}^{\alpha(2)}(z)$ term in Eq. (372) may be completely neglected. Moreover, we shall see below that $\square_{\mathbf{k}}^{\alpha(1)}(z)$ does not contribute to the limiting law term of Eq. (365); we then recover precisely the "plasma" propagator:

$$G^\alpha(\mathbf{k}; z) \simeq 1/(\mathbf{k}\mathbf{v}_\alpha - z) \tag{377}$$

This result gives in fact the mathematical limitation for the validity of the plasma approximation developed in the two preceding sections *even with solvent molecules interacting with the ions, the plasma model will be valid in the limit of Brownian ions, provided that conditions* (376) *holds.*

(2) Another limiting situation is:

$$\zeta_\alpha^2/m_\alpha \geqslant e^2C/\varepsilon \tag{378}$$

corresponding to a large friction. In this case, one has to retain the Brownian operator in Eq. (371) and the calculations have to be developed with the full propagator (371).

From now on, when we talk about a "Brownian approximation" the limit (378) will always be understood.

It is clear that the relevant contributions to the time integral (365) will come, as usual, from the singularities in the z-plane which are close to the real axis. As when γ_α is strictly equal to zero, the singularity of $\tilde{G}(\mathbf{k}; z)$ is a pole at $z = 0$, we shall expand the root of:

$$\mathbf{k}\mathbf{v}_\alpha + \square_{\mathbf{k}}^{\alpha}(z) = z \tag{379}$$

in powers of γ_α, keeping in mind that, from Eq. (376), $\mathbf{k}\mathbf{v}_\alpha$ is at least of order γ_α^2*

$$z = \gamma_\alpha z_1 + \gamma_\alpha^2 z_2 + \ldots \tag{380}$$

* As is shown in Appendix A3, even when $\kappa = O(\gamma_\alpha^n)$, $(n > 1)$—and thus $\mathbf{k}\mathbf{v}_\alpha \ll O(\gamma_\alpha^2)$—we need to keep this term in the root z_1; otherwise we obtain a vanishing result! This is quite reasonable, because the limiting term we are looking for is of the order κ and thus, through the limiting procedure considered here, of order γ_α^n. Retaining this $\mathbf{k}\cdot\mathbf{v}_\alpha$ term whenever $n \geqslant 1$ is thus equivalent to assuming $\mathbf{k}\mathbf{v}_\alpha \sim O(\gamma_\alpha^n)$, as is done here.

Using:

$$\square_{\mathbf{k}}^{\alpha}(z) = \square_{\mathbf{k}}^{\alpha}(0) + \square_{\mathbf{k}}'(0)z + \ldots \tag{381}$$

we then get, identifying equal powers of γ_α;

$$\gamma_\alpha z_1 = \gamma_\alpha \square_{\mathbf{k}}^{\alpha(1)}(0) \tag{382}$$

$$\gamma_\alpha^2 z_2 = \gamma_\alpha^2 \square_{\mathbf{k}}^{\alpha(2)}(0) + \mathbf{k}\mathbf{v}_\alpha + \gamma_\alpha^2 \square_{\mathbf{k}}'^{\alpha(1)}(0)\square_{\mathbf{k}}^{\alpha(1)}(0) \tag{383}$$

However, it is shown in Appendix A2 that

$$\gamma_\alpha \square_{\mathbf{k}}^{\alpha(1)}(0) \equiv 0 \tag{384}$$

while $\gamma_\alpha^2 \square_{\mathbf{k}}^{\alpha(2)}(0)$ is precisely identical to the Fokker–Planck operator (304) calculated for zero wave number.

Summarizing these results, we see that in the limit (378), we have

$$\tilde{G}(\mathbf{k}; z) = \frac{1}{\mathbf{k}\mathbf{v}_\alpha - \square^{\alpha}(0) - z} \tag{385}$$

where the z-independent (Markoffian) collision operator $\square^{\alpha}(0)$ describes the interaction of the heavy ion with the fluid molecules.

Inserting Eq. (385) into Eqs. (365) and (312), it is then easy to obtain the following expression for the current in the Brownian-static approximation:

$$\begin{aligned}\mathbf{J}_1^{(\mathrm{B,s})} = &-\lim_{\tau\to\infty}\sum_\nu \frac{(4\pi e^2 Z_\nu)^2}{8\pi^3\varepsilon^2 kT}\,\frac{eZ_\nu C_\nu}{\zeta_\nu}\int \frac{d\mathbf{k}\,\mathbf{k}}{(k^2+\kappa^2)^2}\left(-\frac{1}{2\pi i}\right)^2 \\ &\times \oint_{C_1} dz_1 \oint_{C_2} dz_2\, \frac{\exp\left[-i(z_1+z_2)\tau\right]}{(z_1+z_2)} \\ &\times \left[e\mathbf{E}Z_\nu \mathbf{J}_\nu'^{\mathrm{B}}(\mathbf{k}; z_1)P'^{\mathrm{B}}(-\mathbf{k}; z_2) + e\mathbf{E}\mathbf{J}'^{\mathrm{B}}(-\mathbf{k}; z_2)P_\nu'^{\mathrm{B}}(\mathbf{k}; z_1)\right]\end{aligned} \tag{386}$$

where we have defined, in analogy to Eqs. (345), (346), and (A31):

$$\mathbf{J}_\nu'^{\mathrm{B}}(\mathbf{k}; z) = \int d\mathbf{p}_\nu \frac{1}{\mathbf{k}\mathbf{v}_\nu - \square^{\nu} - z}\frac{\partial}{\partial \mathbf{p}_\nu}\phi_\nu^{\mathrm{eq.}} \tag{387}$$

$$P_\nu'^{\mathrm{B}}(\mathbf{k}; z) = \int d\mathbf{p}_\nu \frac{1}{\mathbf{k}\mathbf{v}_\nu - \square^{\nu} - z}\phi_\nu^{\mathrm{eq.}} \tag{388}$$

$$\mathbf{J}'^{\mathrm{B}}(\mathbf{k}; z) = \sum_\nu C_\nu Z_\nu^3 \mathbf{J}_\nu'^{\mathrm{B}}(\mathbf{k}; z) \tag{389}$$

$$P'^{\mathrm{B}}(\mathbf{k}; z) = \sum_\nu C_\nu Z_\nu^2 P_\nu'^{\mathrm{B}}(\mathbf{k}; z) \tag{390}$$

As is demonstrated in Appendix A3, the eigenvalues and eigenfunctions of the operator $i(\mathbf{k}\mathbf{v}_\alpha - \Box^\alpha)$ can be calculated exactly: in the limit (378) we may restrict ourselves to the lowest eigenvalue, with the result (see A.70):

$$\mathbf{J}'^{\mathrm{B}}_\nu(\mathbf{k}; z) \simeq i\mathbf{k}/\zeta_\nu \left(-\frac{ik^2}{\zeta_\nu \beta} - z \right), \; P'^{\mathrm{B}}_\nu(\mathbf{k}; z) = 1/\left(-\frac{ik^2}{\zeta_\nu \beta} - z \right) \quad (391)$$

Inserting Eq. (391) into Eq. (386), the remaining integrals are very easy to evaluate. One first integrates over z_1 (the only pole that contributes is $z_1 = -z_2$); the integral over z_2 is calculated by closing the contour C_2 in the upper half-plane; finally, the integral over $\mathbf{k}$ is evaluated, with the result:

$$\mathbf{J}_1^{(\mathrm{B,s})} = \frac{-\pi \mathbf{E} e^6}{3\kappa(\varepsilon k T)^2} \sum_{\mu,\nu} \frac{C_\nu C_\mu}{\zeta_\nu} \left[\frac{Z_\mu^4 Z_\nu^2}{\zeta_\nu \left(\frac{1}{2\zeta_\mu} + \frac{1}{2\zeta_\nu} \right)} - \frac{Z_\nu^3 Z_\mu^3}{\zeta_\mu \left(\frac{1}{2\zeta_\mu} + \frac{1}{2\zeta_\nu} \right)} \right] \quad (392)$$

It should be pointed out that in the case where the two species have the same friction coefficient, this expression is identical with the "plasma static" approximation, Eq. (320).

E. The "Brownian-Dynamic" model: Microscopic Formulation of Onsager Relaxation Theory

From what we have seen above, the plasma-dynamical model of Section V-C provides a rigorous formulation of the relaxation effect under the following conditions:

(a) *Dilute electrolyte* (see Eq. (171)):

$$e^2 C^{1/3}/\varepsilon k T \ll 1 \quad (393)$$

(b) *Heavy ions:*

$$\gamma_\alpha = \sqrt{m_0/m_\alpha} \ll 1 \quad (394)$$

(c) *Small friction:* this condition expresses a link between the two limiting procedures (393) and (394), i.e.

$$\zeta_\alpha^2(m_0)/m_\alpha \ll e^2 C/\varepsilon \quad (395)$$

where we have indicated that ζ_α depends, in principle, upon the solvent mass m_0.

(d) The interactions between solvent-ion and solvent-solvent molecules are short range. More precisely, it is supposed that the

long-range part of these interactions may be entirely incorporated in the dielectric constant ε.

As we have seen in the preceding section, another model may be developed in which condition (c) is replaced by:

(c') *Large friction:*

$$\zeta_\alpha^2(m_0)/m_\alpha \gtrsim e^2C/\varepsilon \tag{396}$$

However, we have not yet treated this latter problem in its full generality because we have used until now the screened Debye potential (314) instead of the correct Coulombic interaction (154).

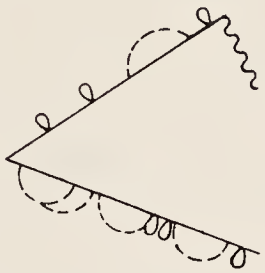

Fig. 16. A typical diagram in the "Brownian-dynamic" model.

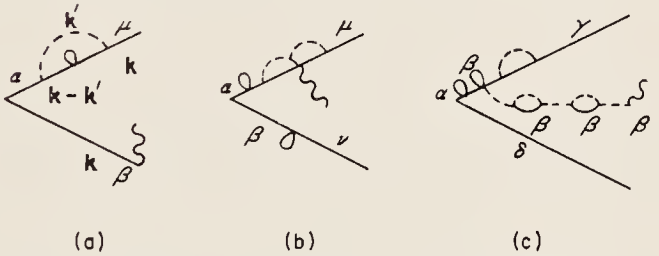

Fig. 17. Diagrams irrelevant to the limiting law.

We want to analyze here the effect of these long-range Coulomb forces in the large friction limit (396); we shall thus consider the "Brownian-dynamic" approximation, which, as we shall see presently, gives exactly the same result as the classical semi-phenomenological theory developed in Section V-A.

It is very easy to find the class of diagrams which have to be retained in order to get the correct relaxation effect; indeed the replacement of the screened potential (314) by the Coulomb law (154) forces us to retain all the ring diagrams in order to eliminate the long-range divergences, precisely as was done in Section V-C. However, we also now have to insert on each "plasma" line the interactions with the solvent, as is illustrated in Fig. 16.

On the other hand, the examples of Fig. 17 give negligible contributions to the limiting law; indeed, Fig. 17a, in which a solvent molecule is excited *during* the interaction between two ions α and μ, is of a less diverging type than Fig. 15 because the wave number exchanged between the two ions is not $\mathbf{k}$ but $(\mathbf{k} - \mathbf{k}')$ (see Eq. (364) for a similar situation). In Fig. 17b, the solvent molecules are interacting with ion μ while this latter ion is accelerated by the field: it was shown in Section IV that this type of contribution was of a higher order in γ_α and may thus be neglected. Finally, the diagram 17c—which was retained in the

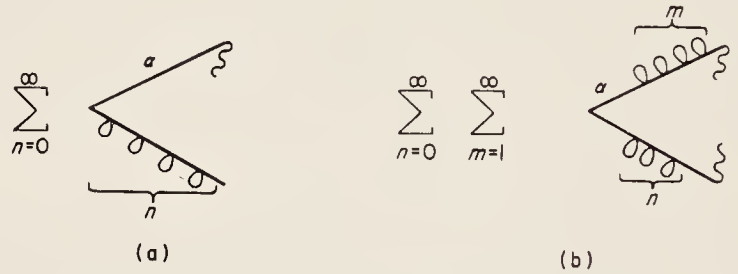

Fig. 18. The two types of contributions to $\mathbf{J}_1^{(\mathrm{B,d})}$.

corresponding plasma approximation (see T_α^{II}, T_α^{IV}, and T_α^{V} in Fig. 13) is negligible because particle β is strongly dissipated by Brownian interaction with the solvent (while in the plasma case, it propagates freely) after its acceleration by the field.

The diagrams of the type shown in Fig. 16 are drawn in Figs. 18a and b, where we have represented separately the terms for which particle α propagates through the whole diagram and the terms where particle α is exchanged. The heavy lines represent Brownian propagators, as in Eq. (185); otherwise these terms are similar to T_α^{I} and T_α^{III}, Fig. 13 and Eqs. (347) and (357). The formal summation is rather long but runs exactly along the same lines as in this latter case; we simply quote the final result:

$$\begin{aligned}\mathbf{J}_1^{(18a)} = &-\lim_{\tau\to\infty}\sum_\nu \frac{eZ_\nu C_\nu}{\zeta_\nu}\frac{(4\pi e^2 Z_\nu)^2}{8\pi^3\varepsilon^2 kT}\int\frac{d\mathbf{k}\,\mathbf{k}}{(k^2+\kappa^2)k^2}\left(-\frac{1}{2\pi i}\right)^2\\ &\times\oint_{C_1}\oint_{C_2} dz_1 dz_2\,\frac{\exp\left[-i(z_1+z_2)\tau\right]}{(z_1+z_2)}\,\frac{1}{[1-J^{\mathrm{B}}(-\mathbf{k};z_2)]}\\ &\times\{e\mathbf{E}Z_\nu\mathbf{J}_\nu'^{\mathrm{B}}(\mathbf{k};z_1)P'^{\mathrm{B}}(-\mathbf{k};z_2)+e\mathbf{E}\mathbf{J}'^{\mathrm{B}}(-\mathbf{k};z_2)P_\nu'^{\mathrm{B}}(\mathbf{k};z_1)\}\end{aligned} \tag{397}$$

and:

$$\mathbf{J}_1^{(18b)} = -\lim_{\tau\to\infty}\sum_\nu \frac{eZ_\nu C_\nu}{\zeta_\nu}\frac{(4\pi e^2 Z_\nu)^2}{8\pi^3\varepsilon^2 kT}\int \frac{d\mathbf{k}\,\mathbf{k}}{(k^2+\kappa^2)k^2}\left(-\frac{1}{2\pi i}\right)^2$$

$$\times \oint_{C_1} dz_1 \oint_{C_2} dz_2 \frac{\exp\left[-i(z_1+z_2)\tau\right]}{z_1+z_2} J_\nu^{\mathrm{B}}(\mathbf{k};z_1)$$

$$\times \frac{1}{[1-J^{\mathrm{B}}(\mathbf{k};z_1)][1-J^{\mathrm{B}}(-\mathbf{k};z_2)]}$$

$$\times \{e\mathbf{E}Z_\nu \mathbf{J}_\nu'^{\mathrm{B}}(\mathbf{k};z_1)P'^{\mathrm{B}}(-\mathbf{k};z_2) + e\mathbf{E}\mathbf{J}'^{\mathrm{B}}(-\mathbf{k};z_2)P_\nu'^{\mathrm{B}}(\mathbf{k};z_1)\} \tag{398}$$

where we have used the definitions (387), (388), (389), and (390) and

$$J_\nu^{\mathrm{B}}(\mathbf{k};z) = \frac{4\pi e^2}{\varepsilon k^2}\int d\mathbf{p}_\nu \frac{1}{\mathbf{k}\mathbf{v}_\nu - \square^\nu - z}\,\mathbf{k}\frac{\partial}{\partial \mathbf{p}_\nu}\phi_\nu^{\mathrm{eq.}} \tag{399}$$

$$J^{\mathrm{B}}(\mathbf{k};z) = \sum_\nu Z_\nu^2 C_\nu J_\nu^{\mathrm{B}}(\mathbf{k};z) \tag{400}$$

As is shown in Appendix A2, we have in the limit of small $\mathbf{k}$:

$$J_\nu^{\mathrm{B}}(\mathbf{k};z) = \frac{4\pi e^2 i}{\varepsilon\zeta_\nu}\frac{1}{\left(-\dfrac{ik^2}{\zeta_\nu\beta}-z\right)} \tag{401}$$

Inserting Eqs. (391) and (401), we can evaluate the integrals over z_1, z_2 and $\mathbf{k}$ without special difficulties. For instance, we have:

$$\mathbf{J}_1^{(18a)} = -\sum_\nu \frac{eZ_\nu C_\nu}{\zeta_\nu}\frac{(4\pi e^2 Z_\nu)^2}{8\pi^3\varepsilon^2 kT}\int \frac{d\mathbf{k}\,\mathbf{k}}{(k^2+\kappa^2)k^2}\left(\frac{1}{2\pi i}\right)\int_{-\infty}^{+\infty} dz_2$$

$$\times \frac{Z_\nu e\mathbf{E}\mathbf{J}_\nu'^{\mathrm{B}}(\mathbf{k};-z_2)P'^{\mathrm{B}}(-\mathbf{k};z_2) + e\mathbf{E}\mathbf{J}'^{\mathrm{B}}(-\mathbf{k};z_2)P_\nu'^{\mathrm{B}}(\mathbf{k};-z_2)}{[1-J^{\mathrm{B}}(-\mathbf{k};z_2)]} \tag{402}$$

Integrating over z_2 by closing the contour in the upper half-plane with a single pole at $z_2 = ik^2/\zeta_\nu\beta$, we get:

$$\mathbf{J}_1^{(18a)} = -\sum_{\nu,\mu} \frac{eZ_\nu C_\nu}{\zeta_\nu} \frac{(4\pi e^2 Z_\nu Z_\mu)^2}{8\pi^3(\varepsilon kT)^2} \int \frac{d\mathbf{k}\mathbf{k}(\mathbf{kE})}{(k^2+\kappa^2)k^2} \times \left\{ \frac{eZ_\nu}{\zeta_\nu} \frac{C_\mu}{\left(\frac{1}{\zeta_\mu}+\frac{1}{\zeta_\nu}\right)} - \frac{eC_\mu Z_\mu}{\zeta_\mu} \frac{Z_\nu}{\left(\frac{1}{\zeta_\mu}+\frac{1}{\zeta_\nu}\right)} \right\} 1 \Big/ \left[k^2 + \frac{4\pi e^2}{\varepsilon kT} \sum_\delta \frac{C_\delta Z_\delta^2}{\zeta_\delta \left(\frac{1}{\zeta_\delta}+\frac{1}{\zeta_\nu}\right)} \right] \tag{403}$$

The $\mathbf{k}$ integral is immediately evaluated (see Eq. (287)) and the result is:

$$\mathbf{J}_1^{(18a)} = -\frac{4\pi}{3\kappa} \frac{\mathbf{E}e^6}{(\varepsilon kT)^2} \frac{C_\alpha C_\beta Z_\alpha^2 Z_\beta^2}{(\zeta_\alpha+\zeta_\beta)} \left[\frac{\zeta_\beta Z_\alpha}{1+q_\alpha} - \frac{\zeta_\alpha Z_\beta}{1+q_\beta} \right] \left(\frac{Z_\alpha}{\zeta_\alpha} - \frac{Z_\beta}{\zeta_\beta} \right) \tag{404}$$

with

$$q_\nu^2 \kappa^2 = \frac{4\pi e^2}{\varepsilon kT} \sum_\delta \frac{C_\delta Z_\delta^2}{\zeta_\delta \left(\frac{1}{\zeta_\delta}+\frac{1}{\zeta_\nu}\right)} \tag{405}$$

The calculation of $\mathbf{J}_1^{(18b)}$ is made in the same fashion. When the two results are added, we recover the well-known Onsager formula:

$$\mathbf{J}_1^{(B,d)} = \mathbf{J}_1^{(18a)} + \mathbf{J}_1^{(18b)} = -\frac{\pi \mathbf{E}e^6}{3\kappa(\varepsilon kT)^2} \frac{4C_\alpha C_\beta Z_\alpha^2 Z_\beta^2 (Z_\alpha - Z_\beta) q^2}{1+q} \left(\frac{Z_\alpha}{\zeta_\alpha} - \frac{Z_\beta}{\zeta_\beta} \right) \tag{406}$$

which may be rewritten as:

$$\mathbf{J}_1^{(B,d)} = -\mathbf{J}_0 \frac{e^2 |Z_\alpha Z_\beta| \kappa}{3\varepsilon kT} \frac{q^2}{1+q} \tag{407}$$

in accordance with Eq. (295).

F. Discussion—Comparison with Other Approaches

In the four preceding sections, we have developed various approximations for the relaxation term in the limiting law for the conductance of electrolytes, starting from the generalized transport equation (111).

In the simplest model, the interactions with the solvent were completely neglected and the collective Coulomb interactions between the ions were imitated by a screened Coulomb potential; the result is (see Eq. (321))

$$\frac{\mathbf{J}_1^{(\mathrm{p,s})}}{\mathbf{J}_0} = -\frac{\kappa e^2}{12\varepsilon kT}\,|Z_\alpha Z_\beta| \tag{408}$$

Another very simple model corresponds to Brownian motion of the ions, with a screened potential; one then has (see Eq. (392))

$$\frac{\mathbf{J}_1^{(\mathrm{B,s})}}{\mathbf{J}_0} = \frac{-e^2\kappa}{12\varepsilon kT}\,|Z_\alpha Z_\beta| 2q^2 \tag{409}$$

with q defined by Eq. (283).

While these two approximations are heuristic, the cases treated in Sections V-C and V-E correspond to well defined mathematical limiting procedures. In both models, one considers a dilute electrolyte (see Eq. (393)) with heavy ions (see Eq. (394)); the difference lies in the relation connecting these two limits. The small friction case, Eq. (395), corresponds to the plasma-dynamic model (Eq. (361)):

$$\frac{\mathbf{J}_1^{(\mathrm{p,d})}}{\mathbf{J}_0} = -\frac{e^2\kappa|Z_\alpha Z_\beta|}{12\varepsilon kT}\,\gamma\left(\frac{m_\alpha}{m_\beta};\frac{Z_\alpha}{Z_\beta}\right) \tag{410}$$

where γ is a complicated function of the ratios of the masses and the charges but its value is typically about one. The large friction case, Eq. (396), corresponds to the Brownian-dynamic model (410):

$$\frac{\mathbf{J}_1^{(\mathrm{B,d})}}{\mathbf{J}_0} = -\frac{e^2\kappa}{12\varepsilon kT}\,|Z_\alpha Z_\beta|\,\frac{4q^2}{1+q} \tag{411}$$

which is precisely Onsager's result.

We do not intend to discuss here the connection of these formulas with experiment;[8] we just wish to point out that, as the concentration of the electrolyte increases, one should, in principle, go from the regime of large friction to the regime of small friction; however, with typical electrolytes, the values of the friction coefficients and of the masses are such that, in the range of high dilution, $\Gamma = e^2\beta C^{1/3}/\varepsilon \ll 1$, the large friction coefficient condition is well satisfied and formula (411) should be very satisfactory. Anyhow, the very close agreement between Eqs. (408), (409), (410), and (411) shows a great insensitivity of the limiting law to the particular model which is considered;

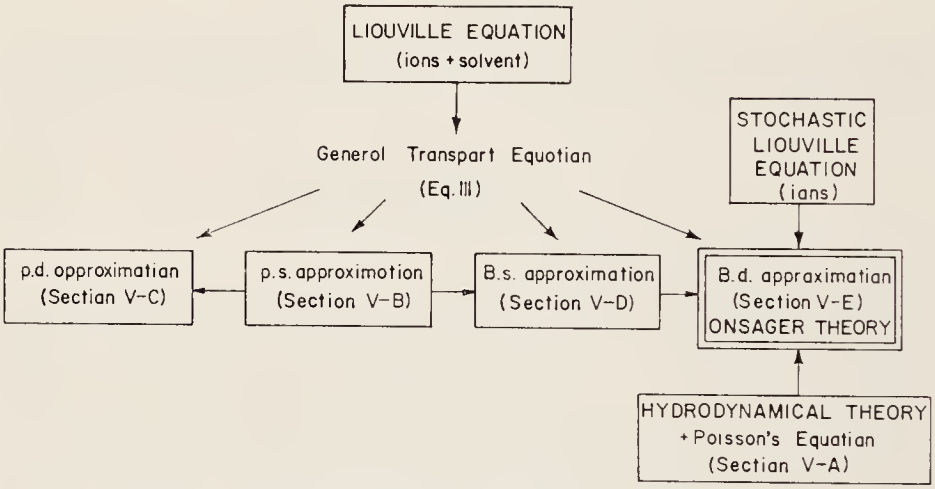

Fig. 19. Logical connection between the theories of the relaxation effect.

this could be a possible indication that the "heavy ion approximation" (394), which was not explicitly used in the derivation of Eqs. (408) and (410), might not be as essential as it appears for the validity of the limiting law. However, a microscopic justification of this assertion would require a better understanding of liquid transport theory than is available now; we shall thus not discuss it any further.

Finally, we wish to close this section by indicating briefly the connection between the present work and other theories of the relaxation effect; this is illustrated in Fig. 19.

In our approach, one starts from the Liouville equation (7) for

the complete system (ions + solvent) and one derives an exact irreversible transport equation (111) for the one particle distribution function of each species; the relaxation effect is isolated in the term of this transport equation describing the acceleration due to the field during a collision process. Various approximations are then developed in order to treat both the long-range Coulomb forces and the interactions between the ions and the solvent; the results of these approximations have been summarized at the beginning of this section; in particular, the "Brownian-dynamic" model gives the well-known Onsager result (411).

Of course, as was shown in Section V-A, this latter expression may also be derived starting from the hydrodynamical equations for the pair distribution and the Poisson equation; it is also the final result of the theories developed independently by Falkenhagen and Ebeling,[9] and by Friedman;[12,13] in these two approaches, the starting point is a Liouville equation for the system of ions with an *ad hoc* stochastic term describing the interactions with the solvent.

However, the present formulation has the advantage of furnishing a mathematically rigorous foundation to the classical theory and is readily extended to other physical situations, like plasmas[32] and semiconductors.* Also, it allows us to give a microscopic foundation to the theory of the electrophoretic effect, which is much more delicate because it involves the difficult question of long-range hydrodynamical correlations: this point will be the object of Section VI.

VI. MICROSCOPIC THEORY OF ELECTROPHORESIS: AN EXAMPLE OF HYDRODYNAMICAL LONG-RANGE FORCES

We have seen in Section V that the classical theory of electrophoresis is intimately connected with the existence of a velocity field of the fluid around a given moving ion, which in turn contributes to a supplementary friction acting on the Debye atmosphere of this ion.

More precisely, it is supposed that the velocity field of the

* See P. Résibois and G. Dewel, *Phys. Letters*, **19**, 360 (1965).

fluid at point $\mathbf{r}$, due to an ion at point $\mathbf{r}_\alpha$ with average velocity $\mathbf{v}_\alpha$, is given by:

$$\mathbf{w}_f(\mathbf{r}) = \boldsymbol{\chi}(\mathbf{r} - \mathbf{r}_\alpha)\mathbf{v}_\alpha \tag{412}$$

where $\boldsymbol{\chi}$ is the divergence-free tensor defined in Eq. (263). An ion located at point $\mathbf{r}$ then feels a supplementary friction force:

$$\delta\mathbf{F}_\beta^{\mathrm{F}}(\mathbf{r}) = -\zeta_\beta \boldsymbol{\chi}(\mathbf{r} - \mathbf{r}_\alpha)\mathbf{v}_\alpha \tag{413}$$

The average velocity $\mathbf{v}_\alpha$ is given, in a first approximation, by $Z_\alpha e\mathbf{E}/\zeta_\alpha$ and ion β has a probability $g_{\alpha\beta}^{\mathrm{eq.}}(\mathbf{r} - \mathbf{r}_\alpha)$ of being at point $\mathbf{r}$ (see Eq. (135)). The average supplementary force is thus:

$$\delta\mathbf{F}_\beta^{\mathrm{F}} = -\zeta_\beta \frac{eZ_\beta \mathbf{E}}{\varepsilon k T} \sum_\alpha \frac{Z_\alpha^2 e^2 C_\alpha}{\zeta_\alpha} \int d\mathbf{r}\, \boldsymbol{\chi}(\mathbf{r}) \frac{\exp(-\kappa r)}{r} \tag{414}$$

$$= -\zeta_\beta e Z_\beta \mathbf{E} \frac{\kappa}{6\pi\eta} \tag{415}$$

where Stokes formula (231) has been used to determine the friction coefficient ζ_α. This simple argument indicates that in order to get a microscopic theory for electrophoresis, it is very useful first to analyze, from the statistical point of view, the velocity field which is created in a fluid when a heavy particle is moving through this fluid. Clearly, this problem is not a simple one, because it involves a careful many-particle description of the fluid, in order to obtain the hydrodynamical long-range effects implied by (412).

We shall see presently that such an analysis is possible, if not with full mathematical rigor at least with the help of physically reasonable arguments.

A. The Velocity Field around a Moving Brownian Particle

We consider a heavy particle of mass m_α located at $\mathbf{r}_\alpha$ and moving with velocity $\mathbf{v}_\alpha$, placed in a fluid of particles of mass m_0 ($\gamma_\alpha = (m_0/m_\alpha) \ll 1$). The Hamiltonian of the system is thus described by Eq. (368).

The conditional velocity of the fluid molecule i, for a given two-particle distribution $f_{i\alpha}(\mathbf{r}_i, \mathbf{r}_\alpha; t)$ is defined by:

$$\mathbf{w}_i(\mathbf{r}_i, \mathbf{r}_\alpha; t) f_{i\alpha}(\mathbf{r}_i, \mathbf{r}_\alpha; t) = \int dp^N dr^{N-1} d\mathbf{p}_\alpha \mathbf{v}_i \rho_{N+1}(\mathbf{r}_\alpha; \mathbf{v}_\alpha; r, v; t) \quad (416)$$

If we look at this velocity field for a large separation $|\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty$ we may replace $f_{i\alpha}$ by its asymptotic form,* namely $1/\Omega^2$, and we then get for the Fourier transform of Eq. (416):

$$\mathbf{w}_i(\mathbf{k}_\alpha, -\mathbf{k}_i; t) = \int dp^N d\mathbf{p}_\alpha \mathbf{v}_i \rho^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\{\mathbf{v}\}; \mathbf{v}_\alpha; t) \quad (417)$$

We consider a stationary distribution, where the velocity distribution of the fluid is at equilibrium:

$$\phi_i(\mathbf{p}_i) = \phi_i^{\text{eq.}} \quad (418)$$

while the heavy particle has a velocity distribution ϕ_α corresponding to a non-vanishing average velocity $\langle \mathbf{v}_\alpha \rangle \neq 0$. We may then apply our general formula, Eq. (88), in its asymptotic form (see also Eq. (93)) to determine $\rho^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}$

$$\mathbf{w}_i(\mathbf{k}_\alpha, -\mathbf{k}_i) = \int dp^N d\mathbf{p}_\alpha \mathbf{v}_i \tilde{\mathscr{C}}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(+i0) \left[\prod_{i=1}^{N} \phi_i^{\text{eq.}}\right] \phi_\alpha \quad (419)$$

where we have here for the creation operator:

$$\mathscr{C}^{+(\alpha i)}_{\mathbf{k},-\mathbf{k}}(+i0) = \left\langle \mathbf{k}_\alpha, -\mathbf{k}_i \middle| \sum_{n=1}^{\infty} \left(\frac{-\lambda}{L_0^\alpha - i0} \delta L^\alpha\right)^n \middle| 0 \right\rangle' \quad (420)$$

and L_0^α, δL^α are defined by Eqs. (225), (226) with the slight and obvious change in notation:

$$L_0^\alpha = L_0^f + \gamma_\alpha L_0^{I,\alpha} \quad (421)$$

$$\delta L^\alpha = \delta L^{f,\alpha} + \gamma_\alpha \delta L^{I,\alpha} \quad (422)$$

We now expand Eq. (420) in power of γ_α; the zeroth-order term gives the equilibrium distribution of the fluid in the presence of the heavy particle: this correlation decays for distances of the order of the short-range molecular forces and may thus be neglected

* We take here the specific pair distribution: the result $f_{i\alpha} \to 1/\Omega^2$ may then easily be demonstrated for distances larger than molecular range, using an argument similar to the one that follows.

in the limit $|\mathbf{r}_\alpha - \mathbf{r}_i| \to \infty$; the first non-trivial term is of order γ_α and is given by (see Eq. (233) for a similar calculation):

$$\gamma_\alpha \tilde{\mathscr{C}}^{+(\alpha i)(1)}_{\mathbf{k},-\mathbf{k}}(+i0) = -\gamma_\alpha \sum_{k'} \left\langle \mathbf{k}_\alpha, -\mathbf{k}_i \right| \frac{1}{L^{f,\alpha} - i0} (L_0^{I,\alpha} + \delta L^{I,\alpha}) \left| k' \right\rangle \rho^{f,\alpha}_{k'} \tag{423}$$

The term involving $\delta L^{I,\alpha}$ gives zero when inserted into Eq. (419) and using Eq. (239) we get:

$$\mathbf{w}_i(\mathbf{k}_\alpha; -\mathbf{k}_i) = -\beta \mathbf{A}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}} \langle \mathbf{v}_\alpha \rangle \tag{424}$$

where the tensor $\mathbf{A}$ is defined by:

$$\mathbf{A}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}} = -i \int dp^N \mathbf{v}_i \sum_{k'} \left\langle \mathbf{k}_\alpha, -\mathbf{k}_i \right| \frac{1}{L^{f,\alpha} - i0} \left| k' \right\rangle (\mathbf{F}^\alpha \rho^{f,\alpha})_{k'} \tag{425}$$

and the force $\mathbf{F}^\alpha$ due to the B-particle has been defined in Eq. (240) and appears here as an external force. Indeed, precisely as in the Brownian motion problem analyzed in Section IV, once the expansion in γ_α has been performed, particle α appears in expressions like (425) only through the forces $\mathbf{F}^{\alpha i}$ and not through its velocity, and is thus similar to a fixed external source of force.

In order to calculate the velocity field (416) far from the B-particle, we need thus to analyze the tensor (425) in the limit of small wave number $\mathbf{k}$.

Let us first put Eq. (425) in the form:

$$\mathbf{A}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}} = \int d\mathbf{p}_i \mathbf{v}_i \boldsymbol{\Phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) \tag{426}$$

where the vector $\boldsymbol{\Phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}$ is defined by

$$\boldsymbol{\Phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \int \prod_{j \neq i} d\mathbf{p}_j \sum_{k'} \left\langle \mathbf{k}_\alpha, -\mathbf{k}_i \right| \frac{1}{L^{f,\alpha} - i0} \left| k' \right\rangle (-i\mathbf{F}^\beta \rho^{f,\alpha})_{k'} \tag{427}$$

We should keep in mind that the velocity of the B-particle does not appear in Eq. (427).

Except for the vector character of the "initial condition", $(-i\mathbf{F}^\alpha \rho^{f,\alpha})_{k'}$, and the fact that here we have $z = i0$, Eq. (427) is similar to expressions we have met previously in deriving transport equations (see for instance Eqs. (38) and (A.36)); the same technique may be applied here and it is possible to write down a transport-like equation for $\boldsymbol{\Phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}$. As the calculations are rather

long but involve nothing new, they have been reported in Appendix 4; we merely quote here the final results. It may be shown from Eq. (427) that $\boldsymbol{\phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}$ obeys the equation:

$$-\mathbf{k}\mathbf{v}_i\boldsymbol{\phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}} - \int \prod_{j\neq i} d\mathbf{p}_j \sum_{k'} \tilde{\tilde{\mathscr{D}}}^{(\alpha i)}_{-\mathbf{k};\mathbf{k}'}(-i\mathbf{F}^{\alpha}\rho^{f,\alpha})_{\mathbf{k}'}$$
$$= \int \prod_{j\neq i} d\mathbf{p}_j \sum_{n\begin{cases}=i\\ \neq i\end{cases}} \langle -\mathbf{k}_i|\Psi(i0)|-\mathbf{k}_n\rangle \boldsymbol{\phi}^{(\alpha n)}_{\mathbf{k},-\mathbf{k}} \prod_{l\neq n} \phi_l^{\text{eq.}} \quad (428)$$

where:

$$\langle \mathbf{k}_i|\Psi(i0)|\mathbf{k}_n\rangle = \sum_{m=1}^{\infty} (-\lambda)^m \left\langle \mathbf{k}_i \middle| \delta L \left(\frac{1}{L_0^f - i0}\, \delta L \right)^m \middle| \mathbf{k}_n \right\rangle' \quad (429)$$

describes the generalized collision operator for the fluid and is characterized by:

(1) *Its irreducibility*: the prime means that the only transitions allowed in Eq. (429) are such that one starts with a single excited particle wave number ($\mathbf{k}_n \neq 0$) and arrives at the final state $\mathbf{k}_i$ without any such intermediate state. As discussed previously in other contexts (see Section II-C), this condition implies that Ψ describes a dynamical process that is localized both in space and time.

(2) *Only fluid interactions appear in* δL. We thus have:

$$\delta L \equiv \sum_{i>j} \delta L^{ij} \quad (430)$$

and no interaction involving the external force created by the B-particle appears in Eq. (429).

As we shall now see, all these latter interactions have been included in the destruction fragment $\tilde{\tilde{\mathscr{D}}}$, which is defined by:

$$\sum_{k'} \tilde{\tilde{\mathscr{D}}}^{(\alpha i)}_{\mathbf{k},-k'}(-i\mathbf{F}^{\alpha}\rho^{f\alpha})_{k'} = \sum_{k'} \sum_{n=0}^{\infty} \left\{ \left\langle \mathbf{k}_i \middle| \left[-\lambda \delta L^{f,\alpha} \frac{1}{L_0^f - i0} \right]^n \middle| k' \right\rangle \right.$$
$$\left. \times\ (-i\mathbf{F}^{\alpha}\rho^{f\alpha})_{k'} \right\}'' \quad (431)$$

where here the *complete* interaction is involved

$$\delta L^{f,\alpha} = \sum_{i>j} \delta L^{ij} + i \sum_j \frac{\partial V^{j\alpha}}{\partial \mathbf{r}_j} \frac{\partial}{\partial \mathbf{p}_j} \quad (432)$$

including the effect of the external force $\partial V^{i\alpha}/\partial \mathbf{r}_i = \mathbf{F}^{\alpha i}$. Moreover, the double prime implies an irreducibility condition that is slightly modified with respect to the previous definitions (as in Eq. (60) for instance). It implies that:

Either (1) all intermediate states involve more than one excited fluid particle (this is just the old definition!),

Or (2) if in some state there is only one fluid particle excited, there will be *on its left* at least one interaction involving the

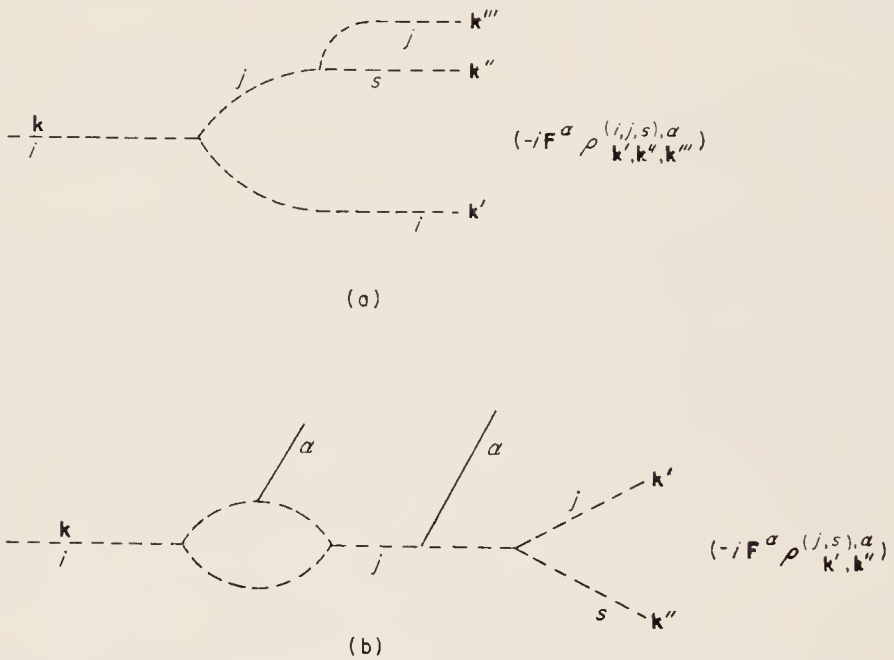

Fig. 20. Example of destruction terms.

external force $\mathbf{F}^{\alpha j}$ $(j = 1, \ldots, N)$. These two situations are respectively illustrated in Figs. 20a and 20b. We recall here that excited fluid particles are represented by dotted lines; moreover, *the static B-particle is not represented here*, except for the forces $\mathbf{F}^{\alpha j}$ which are indicated as plain lines. Indeed, as we have mentioned above, the B-particle plays the role of an external source of force, which automatically adjusts its wave number in such a way that $\mathbf{k}_\alpha = -\sum_j \mathbf{k}_j$ but without any dynamical effect. The reason why the first class of terms is included in the destruction fragment is clear; as the force $\mathbf{F}^\alpha$ appears in the initial condition, this type

of contribution describes molecular processes which are localized in space around the B-particle; similarly, the second class of terms, although it would be reducible with our previous definition, involves collision processes which are also localized around the B-particle because they appear in conjunction with the force $\mathbf{F}^{\alpha j}$.

The conclusion of this discussion is that the Fourier transform of Eq. (431), which we write as:

$$\tilde{\tilde{\mathscr{D}}}^{(\alpha i)}(\mathbf{r}_\alpha, \mathbf{r}_i; \mathbf{p}_i; \{\mathbf{F}^\alpha \rho^{f\alpha}\}) \tag{433}$$

tends to zero rapidly for a separation $|\mathbf{r}_i - \mathbf{r}_\alpha|$ larger than molecular distances. More precisely, we shall suppose that:

$$\tilde{\tilde{\mathscr{D}}}^{(\alpha i)}(\mathbf{r}_\alpha, \mathbf{r}_i; \mathbf{p}_i; \{\mathbf{F}^\alpha \rho^{f\alpha}\}) \leqslant \frac{A}{|\mathbf{r}_i - \mathbf{r}_\alpha|^{2+\varepsilon}}, \ \varepsilon > 0, \ |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{434}$$

Of course a rigorous demonstration of Eq. (434), valid to any order in the coupling constant, is very difficult to obtain. It is, however, easy to obtain for typical low-order terms and we have no reason to believe it should not be correct in general.

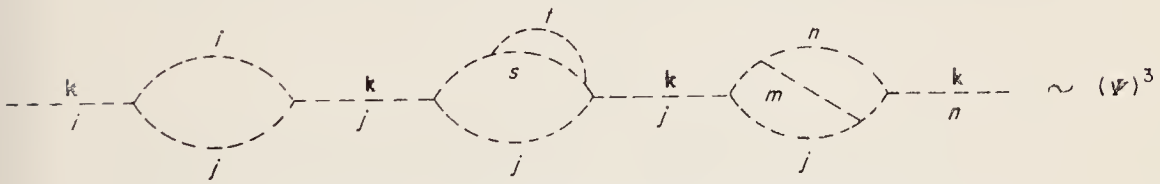

Fig. 21. Example of successive collisions giving rise to long-range effects.

On the contrary, the definition of the collision process, Eq. (429), is such that through a sequence of such events, the perturbation caused by the external force may be propagated at long distances. For instance, in the diagram of Fig. 21, corresponding to a typical term of the iterative solution of Eq. (428), the Ψ operators are not localized around the B-particle. This allows long-range hydrodynamical effects.

As we shall now see, such long-range effects do indeed exist;

we first take the Fourier inverse of the transport-like equation (428) and we obtain the formal result:

$$\mathbf{v}_i \frac{\partial}{\partial \mathbf{r}_i} \boldsymbol{\Phi}^{(\alpha i)}(\mathbf{r}_i, \mathbf{r}_\alpha; \mathbf{p}_i) + i\tilde{\tilde{\mathscr{D}}}^{(\alpha i)}(\mathbf{r}_i, \mathbf{r}_\alpha; \mathbf{p}_i; \{\mathbf{F}^\alpha \rho^{f\alpha}\})$$
$$= i \int \prod_{j \neq i} d\mathbf{p}_j \sum_{n \begin{cases} = i \\ \neq i \end{cases}} \int d\mathbf{r}'_n \Psi(\mathbf{r}_i, \mathbf{r}'_n; \{\mathbf{p}_j\}) \boldsymbol{\Phi}^{(\alpha n)}(\mathbf{r}'_n, \mathbf{r}_\alpha; \mathbf{p}_n) \prod_{l \neq n} \phi_l^{\text{eq.}} \tag{435}$$

where we have used an obvious notation (see Eqs. (14) and (433)) for the Fourier transforms of $\boldsymbol{\Phi}$ and Ψ. The physical interpretation of this equation is clear: on the left-hand side we have the free-flow term and the destruction term which corresponds to local effects around the B-particle; on the right-hand side we find a spatially inhomogeneous collision operator.[36] Also the following condition holds:

$$\lim \boldsymbol{\Phi}^{(\alpha i)}(\mathbf{r}_i; \mathbf{r}_\alpha; \mathbf{p}_i) = 0, \quad |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{436}$$

which expresses the fact that the B-particle does not affect the fluid at infinity; however, if we take large but not infinite distances, $\boldsymbol{\Phi}^{(\alpha i)} \neq 0$, we may hope to find an asymptotic solution to Eq. (435). For such distances, this latter equation becomes:

$$\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} \boldsymbol{\Phi}^{(\alpha i)} - i \int \prod_{j \neq i} d\mathbf{p}_j \sum_n \left[\int d\mathbf{r}'_n \Psi(\mathbf{r}_i, \mathbf{r}'_n; \{\mathbf{p}_j\})(\mathbf{r}_i - \mathbf{r}'_n) \right]$$
$$\times \left(\frac{\partial}{\partial \mathbf{r}_n} \boldsymbol{\Phi}^{(\alpha n)} \right) \prod_{l \neq n} \phi_l^{\text{eq.}} = i \int \prod_{j \neq i} d\mathbf{p}_j \sum_n \Psi_{00}(i0) \boldsymbol{\Phi}^{(\alpha n)} \prod_{l \neq n} \phi_l^{\text{eq.}}$$

for $\quad |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{437}$

where the argument for each $\boldsymbol{\Phi}^{(\alpha n)}$ is $(\mathbf{r}_i, \mathbf{r}_\alpha; \mathbf{p}_n)$. In Eq. (437) we have neglected the destruction term $\tilde{\tilde{\mathscr{D}}}^{(\alpha i)}$ according to Eq. (434) and we have expanded $\boldsymbol{\Phi}^{(\alpha n)}(\mathbf{r}'_n, \mathbf{r}_\alpha; \mathbf{p}_n)$ around $\mathbf{r}'_n \simeq \mathbf{r}_i$; it is then easy to check that the operator $\Psi_{00}(i0)$ appearing on the r.h.s. is precisely the collision process defined by Eq. (75).

If one uses the well-known properties of $\Psi_{00}(i0)$, namely that this operator has five eigenfunctions with zero eigenvalues corresponding to the collision invariants $\sum_i 1$, $\sum_i \mathbf{p}_i$, $\sum_i p_i^2/2m_i$,

it is possible to obtain an asymptotic solution of Eq. (437) in the form:[33]

$$\Phi^{(\alpha n)} = \frac{\Phi^{(\alpha n)(0)}}{r_{\alpha n}} + \frac{\Phi^{(\alpha n)(1)}}{r_{\alpha n}^2} + \cdots \tag{438}$$

However, this method is rather long and it is simpler to notice that if we set:

$$f^i(\mathbf{r}_i - \mathbf{r}_\alpha; \mathbf{p}_i) = \phi_i^{\text{eq.}} - \beta\langle \mathbf{v}_\alpha \rangle \Phi^{(\alpha i)}(\mathbf{r}_i - \mathbf{r}_\alpha; \mathbf{p}_i) \tag{439}$$

Eq. (437) may be transformed into a true transport equation for f^i; this transport equation is the *generalized linearized Boltzmann equation* for f^i, as it also appears in the theory of thermal transport coefficients. More precisely, we get:*

$$\mathbf{v}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} f^i - i \int \prod_{j \neq i} d\mathbf{p}_j \sum_n \left[\int d\mathbf{r}'_n \Psi(\mathbf{r}_i; \mathbf{r}'_n; \mathbf{r}_\alpha; \{\mathbf{p}_j\})(\mathbf{r}_i - \mathbf{r}'_n) \right] \times \left(\frac{\partial}{\partial \mathbf{r}} f^n \right) \prod_{l \neq n} \phi_l^{\text{eq.}} = i \int \prod_{j \neq i} d\mathbf{p}_j \sum_n \Psi_{00}(i0) f^n \prod_{l \neq n} \phi_l^{\text{eq.}}$$

$$\text{for} \qquad |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{440}$$

subject to the asymptotic condition:

$$f^i(\mathbf{r}_i - \mathbf{r}_\alpha; \mathbf{p}_i) = \phi_l^{\text{eq.}} - \frac{\beta\langle \mathbf{v}_\alpha \rangle \Phi^{(\alpha i)(0)}}{|\mathbf{r}_{\alpha i}|} - \frac{\beta\langle \mathbf{v}_\alpha \rangle \Phi^{(\alpha i)(1)}}{|\mathbf{r}_{\alpha i}|^2} + \cdots$$

$$\text{for} \qquad |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{441}$$

The transport equation (441) has been studied in another context;[30,35,36] it is out of place to give this analysis here and we shall merely quote the conclusion: in the case of small gradients, *Eq.* (440) *is entirely equivalent to the well-known Stokes–Navier equation of hydrodynamics.*† More precisely, the average velocity $\mathbf{w}$, which from Eqs. (424), (426), and (439) is given by:

$$\mathbf{w}(\mathbf{r}_i - \mathbf{r}_\alpha) = \int d\mathbf{p}_i \mathbf{v}_i f^i(\mathbf{r}_i - \mathbf{r}_\alpha; \mathbf{p}_i) \tag{442}$$

* This equation is the analogue in the presence of thermal gradients of the transport equation derived in Section II (see Eq. (111)) for the case of an external field.

† This type of argument furnishes in fact the microscopic justification of hydrodynamical equations.

obeys the linearized Stokes–Navier equation:[37]

$$\eta \nabla_{ii}^2 \mathbf{w}_i = \frac{\partial}{\partial \mathbf{r}_i} \mathbf{P}, \quad |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{443}$$

together with the continuity equation, which is here:

$$\frac{\partial}{\partial \mathbf{r}_i} \mathbf{w}_i = 0, \quad |\mathbf{r}_i - \mathbf{r}_\alpha| \to \infty \tag{444}$$

In these equations, η is the shear viscosity of the fluid and $\mathbf{P}$ the pressure tensor; moreover, as they are only valid at large distances, the incompressibility condition has been used (see footnote to page 255).

The two equations (443) and (444) are precisely the starting point of the derivation of Stokes law, given by Eq. (412). As this proof can be found in any textbook on hydrodynamics,[37] we shall not reproduce it here.

From our present point of view, it will suffice to stress that Eqs. (443) and (444) have been obtained here through a microscopic analysis of the N-body problem involving the fluid and the heavy B-particle. We are led to the conclusion that microscopic theory indeed allows us to show that:

$$\mathbf{w}(\mathbf{r}_i - \mathbf{r}_\alpha) = \frac{Q_\alpha}{r_{i\alpha}} \left[\mathbf{U} + \frac{\mathbf{r}_{i\alpha} : \mathbf{r}_{i\alpha}}{r_{i\alpha}^2} \right] \langle \mathbf{v}_\alpha \rangle + O\left(\frac{1}{r_{i\alpha}^2}\right) \tag{445}$$

However, one difference exists with classical theory: in this latter case, the Navier–Stokes equation (443) and the incompressibility condition (444) are assumed to be valid for all distances $r_{i\alpha}$. In this case, it is an easy matter to calculate explicitly the higher-order terms in Eq. (445), and the boundary condition at the B-particle (assumed to be spherical) imposes the condition that:

$$Q_\alpha = R_\alpha \tag{446}$$

This latter point is no longer true in our statistical analysis: indeed, Eqs. (443) and (444) are only true for large distances. From this, we may easily conclude that the asymptotic velocity field has the form (445) but the length Q_α remains undetermined. In order to calculate it explicitly, we would have to solve the

complete inhomogeneous transport equation (435), including the local $\tilde{\tilde{\mathscr{D}}}^{(\alpha i)}$ term; this latter inhomogeneous term replaces the boundary condition of classical theory.

However, such an explicit evaluation of Q_α is very difficult and one can only hope to evaluate it in very simple models; moreover, it is clear from a simple dimensional analysis that the result (443) indeed gives the correct order of magnitude. We shall thus not dwell upon this point any further; rather, after this rather detailed analysis of the velocity field, we shall now consider the problem of electrophoresis.

B. Electrophoresis

We are now in a position which allows us to give a microscopic analysis of electrophoresis. However, the detailed calculations rapidly become extremely complicated and we shall often be obliged to replace strict mathematical proofs by physical plausibility arguments.

Our discussion of Section V has indicated that the electrophoretic effect has to be found in the T_α term defined in Eq. (301) (see also Eq. (312)); moreover we have already found a diagram (Fig. 14a) in which the solvent is transmitting the wave number $-\mathbf{k}$ from ion β to ion α, as we expect to find from the classical theory. This term was not calculated in Section V because it gives a contribution of order e^4 to $\mathbf{J}_1$ while the relaxation term is of order e^6; it will be considered presently.

However, it is clear that this diagram alone cannot describe any kind of long-range hydrodynamical correlations because, as is obvious from the discussion given in the previous section, this effect can only come from a collective description of the solvent.

From the considerations which were used in calculating the velocity field, Eq. (445), it is easy to find a class of terms, of order e^4, which contributes to the limiting law; this class is illustrated in Fig. 22a, where the diagram has been cut in two parts:

(a) To the right of the vertical line, we have Brownian propagation of both ions α and β; their propagators will be described by Eq. (385), because we shall limit ourselves here to the large friction case.

(b) To the left of this line, we have simultaneously the propagation of ion α together with the transmission of the wave number $-\mathbf{k}$ from ion α to ion β through a "box". This box describes the most general process involving the fluid, which starts by a series of interactions with ion α and ends with a series of vertices involving β, without overlapping between these two parts; in other words, the wave number of ion β vanishes before the line of ion α enters

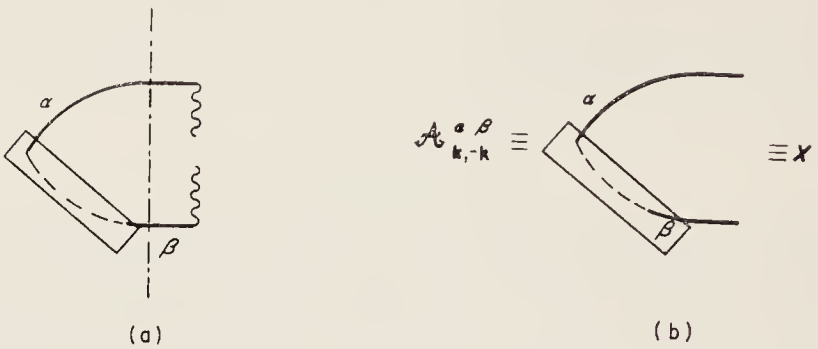

Fig. 22. The diagrams contributing to electrophoresis and the definition of $\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$.

the box. The reason why we only retain this class of terms is that we want to allow long-range propagation by the fluid—as shown in Fig. 21—which is clearly impossible if ions α and β overlap in the box, because this would correspond to "multiple" scattering processes on particles α and β.

Let us call this part to the left of the vertical line $\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$; clearly, its evaluation is the non-trivial part of the problem. Before calculating this term we wish to make two remarks:

(1) the simplest diagram involved in the schematic picture of Fig. 22a is the graph of Fig. 14a; and

(2) if we formally represent $\mathscr{A}^{\alpha\beta}_{\mathbf{k}-\mathbf{k},}$ by a cross ("effective vertex"), the diagram 22a takes the form indicated in Fig. 23, which is very similar to the relaxation graph of Fig. 15. The only difference is that the Debye–Hückel vertex $\delta L^{\alpha\beta}_{\mathrm{D.H}}$ is replaced by the "hydrodynamical vertex" $\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$. This point will be relevant in our discussion of Section VI-C.

According to our general program, we wish to analyze the behavior of $\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$ in the limit of small wave numbers and of small γ_α. Let us systematically expand $\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$ in powers of γ_α:

we first notice that the first vertex of this operator is necessarily of the form:

$$-i\mathbf{F}^{\alpha}\frac{\partial}{\partial \mathbf{p}_{\alpha}} \tag{447}$$

because otherwise we obtain a vanishing contribution to the current, by integration over the fluid velocities (see Eq. (312)).

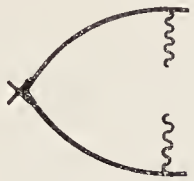

Fig. 23. Formal representation of Fig. 22a.

Secondly, we remark that $\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$ has to involve the velocity of particle β at least once; indeed the zeroth-order term in $\mathbf{v}_{\beta}$ corresponds to a fixed β-particle, in which case of course no hydrodynamical effect appears at all (see remark after Eq. (422)). Moreover this velocity has to come from the expansion of a propagator:

$$\left(\frac{1}{\sum_i \mathbf{k}_i'\mathbf{v}_i - \mathbf{k}\mathbf{v}_{\beta}}\right)^{(1)} \simeq \frac{1}{\sum_i \mathbf{k}_i'\mathbf{v}_i - i0}\,\mathbf{k}\mathbf{v}_{\beta}\,\frac{1}{\sum_i \mathbf{k}_i'\mathbf{v}_i - i0} \tag{448}$$

because the $\partial/\partial\mathbf{v}_{\beta}$ term gives zero by integration over the velocity $\mathbf{v}_{\beta}$.

We thus have:

$$\mathscr{A}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}} = \gamma_{\alpha}\gamma_{\beta}\mathscr{A}^{\alpha\beta(2)}_{\mathbf{k},-\mathbf{k}} + O(\gamma^3) \tag{449}$$

A straightforward but rather long calculation shows that we have (see Eqs. (233)–(238) for a similar development):*

$$\gamma_{\alpha}\gamma_{\beta}\mathscr{A}^{\alpha\beta(2)}_{\mathbf{k},-\mathbf{k}} = -i\frac{\partial}{\partial \mathbf{p}_{\alpha}}\,\zeta^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}\mathbf{v}_{\beta} \tag{450}$$

where the tensor $\zeta^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$ is defined by:

$$\zeta^{\alpha\beta}_{\mathbf{k},-\mathbf{k}} = \beta\int dp^f \left\langle 0 \left| \mathbf{F}^{\alpha}\frac{1}{i(L^{f,\alpha\beta} - i0)}\,\mathbf{F}^{\beta}\rho^{f,\alpha\beta} \right| \mathbf{k}_{\alpha}, -\mathbf{k}_{\beta};\ \{0\} \right\rangle \tag{451}$$

* The factor $-i$ is introduced in such a way that the Fourier inverse of Eq. (451) is real.

In deriving Eq. (451), we have systematically neglected the contributions to the propagator coming from the B-particles, which give a higher-order contribution in γ_α, and we have written, in accordance with Eq. (227):

$$L^{f,\alpha\beta} = L_0^f + \delta L^{f,\alpha\beta} \tag{452}$$

$$\delta L^{f,\alpha\beta} = \sum_{i>j} \delta L^{ij} + i \sum_j \mathbf{F}^{\alpha j} \frac{\partial}{\partial \mathbf{p}_j} + i \sum_j \mathbf{F}^{\beta j} \frac{\partial}{\partial \mathbf{p}_j} \tag{453}$$

i.e. the Liouville operator corresponds to the Hamiltonian of the fluid interacting with the two B-particles α and β. Note that for large separations between α and β, $\rho^{f,\alpha\beta}$ factorizes in a product of terms, respectively depending upon α and upon β.

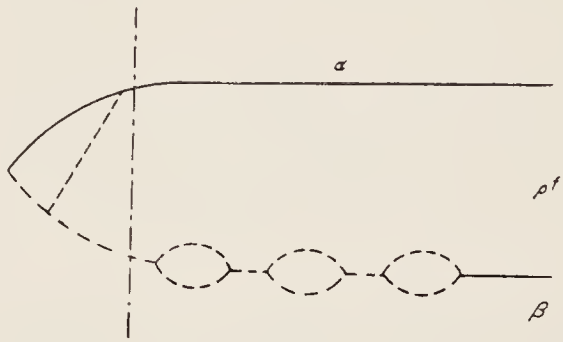

Fig. 24. A typical graph contributing to $\zeta^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$ in the limit of small $\mathbf{k}$.

We should point out here the great analogy between $\zeta^{(\alpha\beta)}_{\mathbf{k},-\mathbf{k}}$ and the friction coefficient ζ studied in the Brownian motion problem of Section IV (see Eq. (242)): instead of having the time autocorrelation function of the force $\mathbf{F}^\alpha$, we now have the time correlation function between $\mathbf{F}^\alpha$ and $\mathbf{F}^\beta$.

We have now to take explicit account of the large separation between ions α and β in order to evaluate Eq. (451). The situation is quite analogous to the problem we had in the previous section when discussing the velocity field (424): here also, the long-range dominant contribution will come from the fluid propagation, as described in Fig. 21, but all vertices involving $\mathbf{F}^{\alpha j}$ (or $\mathbf{F}^{\beta j}$) will be localized around particle α (around particle β). It is thus very natural to retain the graphs of the type indicated in Fig. 24;

it has to be kept in mind in calculating a graph of this type that the heavy particles α and β represented in the diagram are taken as fixed ($\mathbf{v}_\alpha = \mathbf{v}_\beta = 0$; $\partial/\partial\mathbf{v}_\alpha = \partial/\partial\mathbf{v}_\beta = 0$), as is clear from the definitions (451), (452), and (453).

We then separate these graphs into a part involving the forces $\mathbf{F}^{\alpha j}$ and a remainder (see the vertical line in Fig. 24); it is readily realized that this remainder is precisely the vector $\boldsymbol{\Phi}^{(\beta i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i)$ defined in Eq. (427) and we thus have:

$$\boldsymbol{\zeta}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}} = -\beta \sum_i \int d\mathbf{p}_i \mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) \boldsymbol{\Phi}^{(\beta i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) \tag{454}$$

where the "effective" force $\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}$ involves all the interactions where particle α appears and which end with $\mathbf{k}_\alpha - \mathbf{k}_i$; more precisely, we have:

$$\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \int \prod_{l\neq i} d\mathbf{p}_l \left\langle 0 \left| \sum_j \mathbf{F}^{\alpha j} \left[\sum_{n=0}^{\infty} \left(\frac{1}{L_0^f - i0} (-\lambda \delta L^{f,\alpha}) \right)^n \right] \right. \right.$$
$$\left. \left. \rho^{f,\alpha} \right| \mathbf{k}_\alpha, -\mathbf{k}_i \right\rangle'' \prod_{l\neq i} \phi_l^{\text{eq.}} \tag{455}$$

In deriving Eqs. (454) and (455), we have explicitly used the factorization property of $\rho^{f,\alpha\beta}$ for large separations; the double prime in Eq. (455) indicates an irreducibility condition similar to the one used in Eq. (430), except that the words "on its left" have to be replaced by "on its right" in the definition after Eq. (432).

Once Eq. (454) has been obtained, the rest of the analysis is almost trivial from what we already know from the velocity field problem: $\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i)$ is a vector depending on $\mathbf{k}$ and $\mathbf{p}_i$ and it may thus be written as:

$$\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \mathbf{k}\mathscr{V}^{(\alpha i)}(|\mathbf{k}|, |\mathbf{p}_i|, |\mathbf{k}\cdot\mathbf{p}_i|) + \mathbf{p}_i \mathscr{W}^{(\alpha i)}(|\mathbf{k}|, |\mathbf{p}_i|, |\mathbf{k}\cdot\mathbf{p}_i|) \tag{456}$$

where $\mathscr{V}^{(\alpha i)}$ is the Fourier transform of an effective "potential" and $\mathscr{W}^{(\alpha i)}$ has the dimensions of frequency/volume. These two functions depend only on the scalar quantities $|\mathbf{k}|$, $|\mathbf{p}_i|$, $|\mathbf{k}\cdot\mathbf{p}_i|$. Moreover, on a physical basis, we expect that $\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i)$ has a

finite limit for $k = 0$, expressing the short-range character of this effective force; more precisely, we shall need the assumption:

$$\lim_{\mathbf{k}\to 0} \overline{\mathscr{W}}^{(\alpha i)}(|\mathbf{k}|, |\mathbf{p}_i|, |\mathbf{k}\mathbf{p}_i|) = \overline{\mathscr{W}}^{(\alpha i)}(0, |\mathbf{p}_i|, 0) \qquad (457)$$
$$= \text{finite quantity}$$

This property is verified on a simple example in Appendix 5.

The calculation of $\zeta^{\alpha\beta}_{\mathbf{k},-\mathbf{k}}$ can then be performed as for Eq. (426); it can easily be shown that in the limit of small wave numbers:

$$\Phi_{\mathbf{k},-\mathbf{k}} \sim \frac{1}{\Omega}\frac{1}{k^2}\left[\mathbf{U} - \frac{\mathbf{k}\cdot\mathbf{k}}{k^2}\right] + O(k^{-1}) \qquad (458)$$

which is the Fourier inverse of Eq. (445), and we obtain by formal integration* over $\mathbf{p}_i$:

$$\zeta^{\alpha\beta}_{\mathbf{k},-\mathbf{k}} = \frac{\Pi^{\alpha\beta}}{\Omega k^2}\left[\mathbf{U} - \frac{\mathbf{k}:\mathbf{k}}{k^2}\right] + O(k^{-1}) \qquad (459)$$

where $\Pi^{\alpha\beta}$ is $\mathbf{k}$— independent; its evaluation depends on the form of the (unknown) function $\mathscr{W}^{(\alpha i)}(0, |\mathbf{p}_i|, 0)$ and of Q_α (see Eq. (445)). Precisely as in the case of the velocity field, the method we have followed here does not allow us to calculate this constant explicitly; it has however the dimensions of a linear momentum.

Equation (459), together with Eq. (450), is in agreement with classical hydrodynamical theory, except that in this latter case the boundary conditions on the two spheres allow us to set

$$\Pi^{\alpha\beta} = \zeta_\alpha \zeta_\beta / \eta \qquad (460)$$

which is of course the type of result which is expected from a simple dimensional analysis. However, we shall not try to calculate here the constant $\Pi^{\alpha\beta}$ from first principles.

In order to calculate the contribution of the electrophoretic effect to the limiting law, as given by the graph of Fig. 22, the simplest way is to use the above-mentioned analogy between

* Note that the divergence-free character of Eq. (458) implies that $\mathscr{V}^{\alpha i}$ does not contribute to Eq. (459).

the graph of Fig. 23 and that of Fig. 24; we may thus take over the result of Eq. (365), with the substitution:*

$$\langle 0|\delta L^{\alpha\mu}|\mathbf{k}, -\mathbf{k}\rangle \to \mathscr{A}^{(\alpha\mu)}_{\mathbf{k},-\mathbf{k}}$$
$$= \frac{-i}{\Omega}\frac{\partial}{\partial \mathbf{p}_\alpha}\frac{\Pi^{\alpha\beta}}{k^2}\left[\mathbf{U} - \frac{\mathbf{k}:\mathbf{k}}{k^2}\right]\mathbf{v}_\beta + O(k^{-1}) \qquad (461)$$

If we use Eq. (385) for the Laplace transform of the B-propagators, we obtain for the current $\mathbf{J}_1^{\text{El.}}$ (see also Eq. (312)):

$$\mathbf{J}_1^{\text{El.}} = -\lim_{\tau\to\infty}\sum_{\nu,\mu}\frac{4\pi e^2 Z_\nu Z_\mu}{8\pi^3\varepsilon kT}\frac{eZ_\nu C_\nu C_\mu}{\zeta_\nu}\int d\mathbf{p}_\nu d\mathbf{p}_\mu$$
$$\times\int\frac{d\mathbf{k}}{(k^2+\kappa^2)}\left(\frac{-i\Pi^{\nu\mu}}{k^2}\right)\left[\mathbf{U} - \frac{\mathbf{k}:\mathbf{k}}{k^2}\right]\mathbf{v}_\mu\left(-\frac{1}{2\pi i}\right)^2\oint_{C_1}dz_1\oint_{C_2}dz_2$$
$$\times\frac{\exp\left[-i(z_1+z_2)\tau\right]}{(z_1+z_2)}\frac{1}{\mathbf{k}\mathbf{v}_\nu - \square_\nu - z_1}\frac{1}{-\mathbf{k}\mathbf{v}_\mu - \square_\mu - z_2}$$
$$\times\left\{eZ_\nu\mathbf{E}\frac{\partial}{\partial\mathbf{p}_\nu} + eZ_\mu\mathbf{E}\frac{\partial}{\partial\mathbf{p}_\mu}\right\}\phi_\nu^{\text{eq.}}\phi_\mu^{\text{eq.}} \qquad (462)$$

This expression may be rewritten formally as:

$$\mathbf{J}_1^{\text{El.}} = i\lim_{\tau\to\infty}\sum_\nu\frac{4\pi e^2 Z_\nu^2 C_\nu}{8\pi^3\varepsilon kT\zeta_\nu}\int\frac{d\mathbf{k}}{k^2+\kappa^2)k^2}\left(\frac{1}{2\pi i}\right)^2\oint_{C_1}\oint_{C_2}dz_1dz_2$$
$$\times\frac{\exp\left[-i(z_1+z_2)\tau\right]}{(z_1+z_2)}\left\{\left[eZ_\nu\mathbf{E}J_\nu'^{\text{B}}(\mathbf{k};z_1)\right]\cdot\left[\mathbf{U} - \frac{\mathbf{k}:\mathbf{k}}{k^2}\right]\right.$$
$$\left.\times\left[\mathbf{H}_\nu^{\text{B}}(-\mathbf{k};z_2)\right] + \left[\left(\mathbf{U} - \frac{\mathbf{k}:\mathbf{k}}{k^2}\right):\mathbf{L}_\nu^{\text{B}}(-\mathbf{k};z_2)\cdot\mathbf{E}\right]p_\nu'(\mathbf{k};z_1)\right\} \qquad (463)$$

* Note that the divergence of the hydrodynamical force at small k ($\sim k^{-2}$) is stronger than in the Coulomb case ($\sim k^{-1}$); the integral over the velocities is however different, and, as we shall now see, we obtain here also a contribution to the current proportional to $C^{3/2}$.

where the tensorial contractions have been explicitly indicated. Moreover, we have used the definitions:

$$\mathbf{H}_{\nu}^{\mathrm{B}}(\mathbf{k}; z) = \sum_{\mu} e Z_{\mu} C_{\mu} \Pi^{\nu\mu} \int d\mathbf{p}_{\mu} \mathbf{v}_{\mu} \frac{1}{\mathbf{k}\mathbf{v}_{\mu} - \square_{\mu} - z} \phi_{\mu}^{\mathrm{eq.}} \tag{464}$$

$$\mathbf{L}_{\nu}^{\mathrm{B}}(\mathbf{k}; z) = \sum_{\mu} C^2 Z_{\mu}^2 C_{\mu} \Pi^{\nu\mu} \int d\mathbf{p}_{\mu} \mathbf{v}_{\mu} \frac{1}{\mathbf{k}\mathbf{v}_{\mu} - \square_{\mu} - z} \frac{\partial}{\partial \mathbf{p}_{\mu}} \phi_{\mu}^{\mathrm{eq.}} \tag{465}$$

and the previous notation, Eqs. (387) and (388).

We show in Appendix 3 that we have in the limit of small $\mathbf{k}$:

$$\mathbf{H}_{\nu}^{\mathrm{B}}(\mathbf{k}; z) = -i \sum_{\mu} e Z_{\mu} C_{\mu} \Pi^{\mu\nu} \frac{\mathbf{k}}{\beta \zeta_{\mu} \left(\dfrac{-ik^2}{\zeta_{\mu} \beta} - z \right)} \tag{466}$$

which implies that the first term in the bracket of Eq. (463) is zero, while

$$\mathbf{L}_{\nu}^{\mathrm{B}}(\mathbf{k}; z) = -\sum_{\mu} e^2 Z^2{}_{\mu} C_{\mu} \Pi^{\mu\nu} \frac{\mathbf{U}}{m_{\mu} \left(\dfrac{-i\zeta_{\mu}}{m_{\mu}} - z \right)} \tag{467}$$

where $\mathbf{U}$ is the unit tensor. When this latter result is inserted into Eq. (463), the integrations over ζ_1, ζ_2, and $\mathbf{k}$ are easily performed (see the remarks after Eq. (293)); the final expression is:

$$\mathbf{J}_1^{\mathrm{El.}} = -\frac{\mathbf{E}}{6\pi\kappa} \sum_{\mu,\nu} \frac{\Pi^{\nu\mu}}{\zeta_{\nu}\zeta_{\mu}} \frac{4\pi e^2 Z_{\nu}^2 C_{\nu}}{\varepsilon k T} e^2 Z_{\mu}^2 C_{\mu} \tag{468}$$

In the case where the classical assumption (460) is valid, we thus recover the usual result (298).

C. Discussion

Having now found the classical electrophoretic term from a microscopic analysis of the system ions plus solvent, we should analyze more complicated diagrams in order to see whether there is any other contribution than (468) in the limiting form of the electrophoretic term. Indeed, it is very tempting to develop an analysis similar to the one followed in the study of the relaxation term and to consider the possibility of more complicated collective effects. These would have essentially three origins:

(1°) *Collective Coulomb interactions.* We should consider the whole class of ring diagrams generated by the simple diagrams of Fig. 23, as is illustrated in Fig. 25a.

(2°) *Collective hydrodynamical interactions.* We have seen that the long-range hydrodynamical force is diverging at small wave numbers; this suggests very much that one should consider

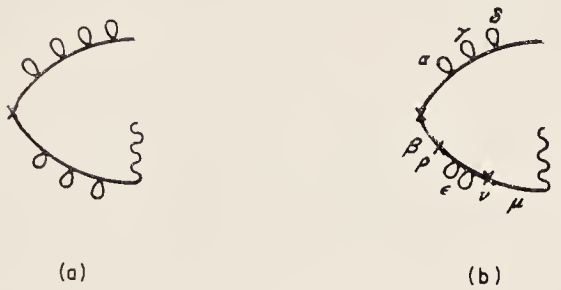

Fig. 25. Coulombic and hydrodynamical collective effects.

also the sum of "ring diagrams" involving "cross vertices" as defined in Fig. 22b: an example of this situation is furnished in Fig. 25b.

(3°) *Non-pairwise hydrodynamical forces.* We should finally take into account hydrodynamical interactions between two particles where, in some intermediate states, we would have a temporary excitation of ions. This type of effect would lead to a kind of "effective" hydrodynamical force and is indicated in Fig. 26.

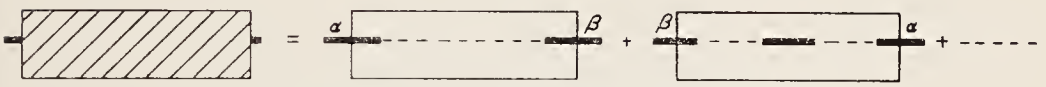

Fig. 26. Effective, non-pairwise, hydrodynamical force.

However, the central result of our above analysis has been that two-particle long-range hydrodynamical effects could be represented by a non-Hamiltonian Markoffian force which has the Fourier transform (see Eq. (461)):

$$\mathbf{F}^{\alpha\beta}_{\mathbf{k},-\mathbf{k}} = \frac{1}{\Omega}\frac{\Pi^{\alpha\beta}}{k^2}\left[\mathbf{U} - \frac{\mathbf{k}:\mathbf{k}}{k^2}\right]\mathbf{v}_\beta + O(k^{-1}) \tag{469}$$

Although the detailed calculations will not be reproduced here, it has been shown recently[16] that a similar result will hold in the

more complicated examples considered in Figs. 25 and 26. Moreover, this form (469) for the two-body Stokes force was the starting point of a very careful analysis by H. L. Friedman[12,13] in which he calculated the contributions to the limiting law coming from these three above-mentioned "many-ion" effects; surprisingly enough, he obtained the result that the sums of these effects cancel each other in the limiting law, which is thus correctly given by Eq. (468).*

VII. APPENDICES

Appendix 1. Explicit Calculation in the "Plasma-Dynamic" Approximation

We present here the detailed calculation of one of the contributions to $\mathbf{J}^{I(p,d)}$.

From Eqs. (312) and (347), we have:

$$\int d\mathbf{p}_\alpha \mathbf{p}_\alpha T_\alpha^I(\mathbf{p}_\alpha) = \frac{4\pi^2 e^2 Z_\alpha^2 \beta}{8\pi^3 \varepsilon^2} \int d\mathbf{p}_\alpha \int \frac{d\mathbf{k}}{(k^2+\kappa^2)} \frac{\mathbf{k}}{k^2} [1 - J^+(-\mathbf{k}; -\mathbf{k}\mathbf{v}_\alpha)]^{-1}$$

$$\times \left[P'(-\mathbf{k}; -\mathbf{k}\cdot\mathbf{v}_\alpha) Z_\alpha e \mathbf{E} \cdot \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial \mathbf{p}_\alpha} + \mathbf{E}\mathbf{J}'(-\mathbf{k}; -\mathbf{k}\cdot\mathbf{v}_\alpha) \phi_\alpha^{\text{eq.}} \right] \quad \text{(A.1)}$$

where J^+, P' and $\mathbf{J}'$ are respectively defined by Eqs. (342), (345), and (347).

It is readily seen that one has:

$$J^+(\mathbf{k}, \mathbf{k}\cdot\mathbf{v}_\alpha) = -\frac{\kappa^2}{k^2} j(w_\alpha) \quad \text{(A.2)}$$

where the variable $w_\alpha = \mathbf{1}_k \cdot \mathbf{v}_\alpha$ has been introduced, and where we have set:

$$j(w_\alpha) = \sum_\mu \theta_\mu^2 \int d\mathbf{p}_\mu \frac{1}{\mathbf{1}_k \mathbf{v}_\mu - w_\alpha - i0} \mathbf{1}_k \cdot \mathbf{p}_\mu \phi_\mu^{\text{eq.}} \quad \text{(A.3)}$$

* After the writing of this article, the problem of limiting viscosity was also considered;[16] although the potential part of the shear viscosity plays the important role, the method developed here can be applied as well; the results are in agreement with the theory of Falkenhagen.[8,16]

with the Debye length of ion μ, characterized by the parameter θ_μ,

$$\kappa_\mu^{-1} = \kappa^{-1}\theta_\mu^{-1} = \left(\frac{4\pi e^2 \beta Z_\mu^2 C_\mu}{\varepsilon}\right)^{-\frac{1}{2}} \tag{A.4}$$

Similarly we have:

$$P'(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha) = \frac{1}{k} p'(w_\alpha) \tag{A.5}$$

with

$$p'(w_\alpha) = \sum_\mu e^2 Z_\mu^2 C_\mu \int d\mathbf{p}_\mu \frac{1}{\mathbf{1}_k \mathbf{v}_\mu - w_\alpha - i0} \phi_\mu^{\text{eq.}} \tag{A.6}$$

while:

$$\mathbf{J}'(\mathbf{k}; \mathbf{k}\mathbf{v}_\alpha) = -\frac{\mathbf{k}}{k^2} j'(w_\alpha) \tag{A.7}$$

with

$$j'(w_\alpha) = \sum_\mu e^3 Z_\mu^3 C_\mu \beta \int d\mathbf{p}_\mu \frac{1}{\mathbf{1}_k \mathbf{v}_\mu - w_\alpha - i0} \mathbf{1}_k \cdot \mathbf{v}_\mu \phi_\mu^{\text{eq.}} \tag{A.8}$$

Some more information may be obtained about the functions j, p', and j' by noticing that:

$$1/(x - i0) = P(1/x) + i\pi\delta(x) \tag{A.9}$$

where $\mathscr{P}$ denotes the Cauchy principal part and $\delta(x)$ is the well-known Dirac delta function. We thus have, for instance:

$$j(w_\alpha) = \sum_\mu \theta_\mu^2 \int_{-\infty}^{+\infty} dp_z \left[\mathscr{P}\left(\frac{1}{v_z - w_\alpha}\right) + i\pi\delta(v_z - w_\alpha)\right] \times v_z \phi_{\mu,z}^{\text{eq.}} \tag{A.10}$$

by taking a system of coordinates with p_z along $\mathbf{1}_k$ and performing the trivial integrations over p_x and p_y. We may rewrite Eq. (A.10) as:

$$j(w_\alpha) = [\bar{\jmath}(w_\alpha) + i\bar{\bar{\jmath}}(w_\alpha)] \tag{A.11}$$

where

$$\bar{\jmath}(w_\alpha) = 1 - \frac{w_\alpha}{\pi^{1/2}} \sum_\mu \theta_\mu^2 g_\mu \int_{-\infty}^{+\infty} dx \, \mathscr{P}\left(\frac{1}{x - g_\mu w_\alpha}\right) \exp(-x^2) \tag{A.12}$$

and

$$\bar{\bar{\jmath}}(w_\alpha) = w_\alpha \pi^{1/2} \sum_\mu \theta_\mu^2 g_\mu \exp(-g_\mu^2 w_\alpha^2) \tag{A.13}$$

are real and *respectively even positive and odd functions of the variable* w_α; the parameter $g_\mu^{-1} = (m_\mu/(2kT)^{1/2})^{-1}$ is a characteristic parameter of the velocity of the particle μ.

Similarly one has:

$$p'(w_\alpha) = \bar{p}'(w_\alpha) + i\bar{\bar{p}}'(w_\alpha) \tag{A.14}$$

where

$$\bar{p}'(w_\alpha) = \frac{1}{\pi^{1/2}} \sum_\mu e^2 C_\mu Z_\mu^2 g_\mu \int_{-\infty}^{+\infty} dx \, \mathscr{P}\left(\frac{1}{x - g_\mu w_\alpha}\right) \exp(-x^2) \tag{A.15}$$

and:

$$\bar{\bar{p}}'(w_\alpha) = \pi^{1/2} \sum_\mu e^2 C_\mu Z_\mu^2 g_\mu \exp(-g_\mu^2 w_\alpha^2) \tag{A.16}$$

Finally, we get:

$$j'(w_\alpha) = \bar{j}'(w_\alpha) + i\bar{\bar{j}}'(w_\alpha) \tag{A.17}$$

where

$$j'(w_\alpha) = \sum_\mu e^3 C_\mu Z_\mu^3 \beta \left[1 - \frac{w_\alpha g_\mu}{\pi^{1/2}} \int_{-\infty}^{+\infty} dx \, \mathscr{P}\left(\frac{1}{x - g_\mu w_\alpha}\right) \exp(-x^2)\right] \tag{A.18}$$

and

$$\bar{\bar{j}}'(w_\alpha) = \pi^{1/2} \sum_\mu e^3 Z_\mu^3 C_\mu \beta g_\mu \exp(-g_\mu^2 w_\alpha^2) \tag{A.19}$$

After these preliminaries, we may start integrating (A.1); we set

$$\alpha_1 = (4\pi e Z_\alpha)^2 \beta/(8\pi^3)\varepsilon^2 \tag{A.20}$$

and we write:

$$\int d\mathbf{p}_\alpha \mathbf{p}_\alpha T_\alpha^I(\mathbf{p}_\alpha) = \alpha_1 \int d\mathbf{p}_\alpha \int d\mathbf{k} \, \frac{1}{(k^2 + \kappa^2)} \, \frac{\mathbf{k}}{k^2} \, \frac{1}{[1 + \kappa^2 j(-w_\alpha)/k^2]}$$
$$\times \left[\frac{1}{k} p'(-w_\alpha) Z_\alpha e \mathbf{E} \, \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial \mathbf{p}_\alpha} + \mathbf{E}\mathbf{k} j'(-w_\alpha) \phi_\alpha^{\text{eq.}}\right] \tag{A.21}$$

We then write:

$$\int d\mathbf{k} = \int d\Omega_k \int_0^\infty k^2 dk; \quad \int d\mathbf{p}_\alpha = \int d\mathbf{p}_{\alpha\perp} \int m_\alpha dw_\alpha \tag{A.22}$$

where we perform the $\mathbf{p}_\alpha$ integration before the $\mathbf{k}$ integration and choose the $p_{\alpha z}$ axis along $\mathbf{1}_k$, thus introducing the element of integration $m_\alpha dw_\alpha$.

The integration over $dp_{\alpha\perp}$ is trivial and we obtain:

$$\int d\mathbf{p}_\alpha \mathbf{p}_\alpha T_\alpha^I(\mathbf{p}_\alpha) = \alpha_1 m_\alpha \int d\Omega_k (\mathbf{1}_k \mathbf{E}) \mathbf{1}_k \int_0^\infty \frac{k^2 dk}{(k^2+\kappa^2)} \times \int_{-\infty}^{+\infty} dw_\alpha \frac{1}{[k^2+\kappa^2 j(-w_\alpha)]} \left[p'(-w_\alpha) \frac{Z_\alpha e}{m_\alpha} \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial w_\alpha}(w_\alpha) + j'(-w_\alpha)\phi_\alpha^{\text{eq.}}(w_\alpha) \right] \tag{A.23}$$

The integrals over Ω_k and w_α are now decoupled; using

$$\int d\Omega_k (\mathbf{1}_k \mathbf{E}) \mathbf{1}_k = \frac{4\pi}{3} \mathbf{E} \tag{A.24}$$

we thus obtain

$$\int d\mathbf{p}_\alpha \mathbf{p}_\alpha T_\alpha^I(\mathbf{p}_\alpha) = \frac{2\pi}{3} \alpha_1 \int_{-\infty}^{+\infty} dw_\alpha \left[p'(-w_\alpha) \frac{Z_\alpha e}{m_\alpha} \frac{\partial \phi_\alpha^{\text{eq.}}}{\partial w_\alpha} + j'(-w_\alpha)\phi_\alpha^{\text{eq.}}(w_\alpha) \right] \int_{-\infty}^{+\infty} \frac{k^2 dk}{(k^2+\kappa^2)[k^2+\kappa^2 j(-w_\alpha)]} \tag{A.25}$$

The integration over k is done by residue calculations:

$$\int \frac{k^2 dk}{(k^2+\kappa^2)(k^2+\kappa^2 j(-w_\alpha)} \equiv \frac{\pi}{\kappa} \frac{1}{(1+\sqrt{{}_+j(-w_\alpha)})} \tag{A.26}$$

where by $\sqrt{{}_+j(-w_\alpha)}$ we denote the determination for the square root of $j(-w_\alpha)$ which has a *positive real part* (see Fig. A.1). The

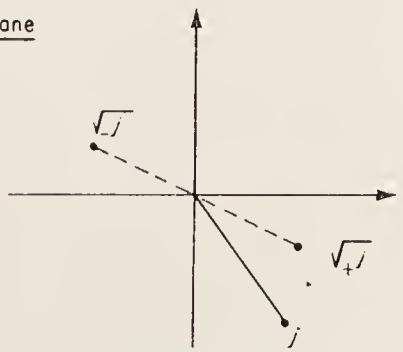

Fig. A.1. The determinations of $\sqrt{j}$.

following procedure is then applied: decompose $\bar{p}'$, $\bar{j}'$ according to Eqs. (A.14) and (A.17) and take the parity of the various parts into account to obtain:

$$\int d\mathbf{p}_\alpha \mathbf{p} T_\alpha^I(\mathbf{p}_\alpha) = \frac{4\pi^2 \alpha_1 m_\alpha}{3\kappa} \mathbf{E} \int_0^\infty dw_\alpha \phi_\alpha^{\text{eq.}} \times \left\{ [\bar{p}'(w_\alpha) Z_\alpha e\beta w_\alpha + \bar{j}(w_\alpha)] \operatorname{Re} \frac{1}{1 + \sqrt{{}_+\bar{j}(w)}} - [\bar{\bar{p}}'(w_\alpha) Z_\alpha e\beta w_\alpha + \bar{\bar{j}}(w_\alpha)] \operatorname{Im} \frac{1}{1 + \sqrt{{}_+\bar{j}(w)}} \right\} \quad \text{(A.27)}$$

The real and imaginary parts of $(1 + \sqrt{{}_+\bar{j}(w)})^{-1}$ may be explicitly evaluated; for $w_\alpha > 0$, one has, after some tricky calculations:

$$\operatorname{Re} \frac{1}{1 + \sqrt{{}_+\bar{j}(w)}} = \frac{(1-\bar{j})[\bar{j} - (\sqrt{2})^{-1}(\bar{j} + \sqrt{\bar{j}^2 + \bar{\bar{j}}^2})^{1/2}] - \bar{\bar{j}}(\bar{\bar{j}} + \sqrt{\bar{j}^2 + \bar{\bar{j}}^2} - 1)^{1/2}}{(1-\bar{j})^2 + \bar{\bar{j}}^2} + 1 \quad \text{(A.28)}$$

$$\operatorname{Im} \frac{1}{1 + \sqrt{{}_+\bar{j}(w)}} = \frac{(1-\bar{j})[\bar{\bar{j}} - (\sqrt{2})^{-1}(\sqrt{\bar{j}^2 + \bar{\bar{j}}^2} - 1)^{1/2}] + \bar{\bar{j}}[1 - (\sqrt{2})^{-1}(\bar{j} + \sqrt{\bar{j}^2 + \bar{\bar{j}}^2})}{(1-\bar{j})^2 + \bar{\bar{j}}^2} \quad \text{(A.29)}$$

Note that if we completely neglect the velocity-dependent factor in (A.11), we have simply:

$$\operatorname{Re} \frac{1}{1 + \sqrt{{}_+\bar{j}}} \simeq \frac{1}{2}, \quad \operatorname{Im} \frac{1}{1 + \sqrt{{}_+\bar{j}}} \simeq 0 \quad \text{(A.30)}$$

With Eqs. (A.27), (A.28), and (A.29), we now have all the elements necessary for a numerical calculation: $\bar{p}'$, $\bar{\bar{p}}'$, $\bar{j}'$, $\bar{\bar{j}}'$, $\bar{j}$, and $\bar{\bar{j}}$ are indeed easily computed from tables on plasma functions.[10]

If we introduce Eq. (A.27) into Eq. (312), and use the definitions:

$$\bar{p}'(w_\alpha) \equiv \sum_\mu e^2 Z_\mu^2 C_\mu \bar{p}'_\mu(w_\alpha)$$
$$\bar{j}'(w_\alpha) \equiv \sum_\mu e^3 Z_\mu^3 C_\mu \bar{j}'_\mu(w_\alpha) \quad \text{(A.31)}$$

we obtain another useful form:

$$\mathbf{J}_1^{\mp(\mathrm{p.d})} = -\mathbf{E}\,\frac{e^6\pi}{3\kappa(kT)^2}\sum_{\mu,\nu}\frac{C_\nu C_\mu}{\zeta_\nu}\,(Z_\mu^2 Z_\nu^4 A_{\nu\mu} - Z_\mu^3 Z_\nu^3 B_{\nu\mu})$$

where

$$A_{\nu\mu} = -8m_\nu\int_0^\infty dw_\nu \phi_\nu^{\mathrm{eq.}}(w_\nu)\left[\bar{\bar{p}}'_\mu(w_\nu)w_\nu\,\mathrm{Re}\,\frac{1}{1+\sqrt{{}_+j(w_\nu)}}\right.$$
$$\left. - \bar{\bar{p}}'(w_\nu)w_\nu\,\mathrm{Im}\,\frac{1}{1+\sqrt{{}_+j(w_\nu)}}\right] \qquad \text{(A.33)}$$

$$B_{\nu\mu} = 8m_\nu\int_0^\infty dw_\nu \phi_\nu^{\mathrm{eq.}}\left[\bar{\bar{j}}'_\mu(w_\nu)\,\mathrm{Re}\,\frac{1}{1+\sqrt{{}_+j(w_\nu)}}\right.$$
$$\left. - \bar{\bar{j}}'_\mu(w_\nu)\,\mathrm{Im}\,\frac{1}{1+\sqrt{{}_+j(w_\nu)}}\right] \qquad \text{(A.34)}$$

Here again, the functions $A_{\mu\nu}$ and $B_{\mu\nu}$ have to be computed numerically; however this form is interesting because if we use the approximation (A.30), these integrals may be obtained in closed form and, for equal masses $m_\nu = m_\mu$, we easily get:

$$A_{\nu\mu} = 1,\ B_{\nu\mu} = 1 \qquad \text{(A.35)}$$

i.e. we recover the result (320) of the plasma-static approximation.

As a matter of fact, the exact values of Eqs. (A.33) and (A.34) may be shown to remain approximately around the value given by Eq. (A.35) for reasonable values of the masses. Similarly, the other contributions to $\mathbf{J}_1^{(\mathrm{p.d})}$ coming respectively from the explicit evaluation of Eqs. (348), (357), (358), and (359) give only a small correction to Eqs. (A.32) and we thus see that the static approximation gives a qualitatively satisfactory answer, although obtained by much more elementary methods than the ones used in the dynamical approach.

Appendix 2. The Inhomogeneous Fokker-Planck Operator

We wish to demonstrate here Eqs. (371), (384), and (385); however, as many steps in the calculations are similar to the homogeneous Brownian motion problem analyzed in Section IV, we shall be very brief.

We first expand Eq. (367) in powers of λ:

$$\tilde{G}^{\alpha}(\mathbf{k}; z) = \int \prod_{i=1}^{N_0} d\mathbf{p}_i \Big\langle \mathbf{k}_\alpha, \{0\} \Big| \sum_{n=0}^{\infty} \frac{1}{L_0^\alpha - z} \left(-\lambda \delta L^\alpha \frac{1}{L_0^\alpha - z} \right)^n \Big| \mathbf{k}_\alpha, \{0\} \Big\rangle \prod_{i=1}^{N_0} \phi_i^{\text{eq.}} \tag{A.36}$$

which we then reclassify in terms of the number of irreducible transitions $|\mathbf{k}_\alpha, \{0\}\rangle \rightarrow |\mathbf{k}_\alpha, \{0\}\rangle$:

$$\tilde{G}^{\alpha}(\mathbf{k}, z) = \int \prod_{i=1}^{N_0} d\mathbf{p}_i \frac{1}{\mathbf{k}\mathbf{v}_\alpha - z} \sum_{m=0}^{\infty} \left[\langle \mathbf{k}_\alpha, \{0\} | \Psi'(z) | \mathbf{k}_\alpha, \{0\} \rangle \times \frac{1}{\mathbf{k}\mathbf{v}_\alpha - z} \right]^m \prod_{i=1}^{N_0} \phi_i^{\text{eq.}} \tag{A.37}$$

or

$$\tilde{G}^{\alpha}(\mathbf{k}; z) = \frac{1}{\mathbf{k}\mathbf{v}_\alpha - \square_{\mathbf{k}}^{\alpha}(z) - z} \tag{A.38}$$

which is precisely Eq. (371), with the definitions:

$$\langle \mathbf{k}_\alpha, \{0\} | \Psi'(z) | \mathbf{k}_\alpha, \{0\} \rangle = \left\langle \mathbf{k}_\alpha, \{0\} \right| -\lambda \delta L^\alpha \sum_{n=1}^{\infty} \left(\frac{-\lambda}{L_0^\alpha - z} \delta L^\alpha \right)^n \left| \mathbf{k}_\alpha, \{0\} \right\rangle' \tag{A.39}$$

(the prime means that all intermediate states are different from $|\mathbf{k}_\alpha, \{0\}\rangle$) and:

$$\square_{\mathbf{k}}^{\alpha}(z) = \int \prod_{i=1}^{N_0} d\mathbf{p}_i \langle \mathbf{k}_\alpha, \{0\} | \Psi'(z) | \mathbf{k}_\alpha, \{0\} \rangle \prod_i \phi_i^{\text{eq.}} \tag{A.39'}$$

In going from Eq. (A.37) to Eq. (A.38), we have explicitly taken into account that the same solvent molecule does not appear in two successive collisions when the thermodynamic limit ($N \rightarrow \infty$, $\Omega \rightarrow \infty$, $N/\Omega = C$ finite) is taken.

In order to analyze Eq. (A.39) in the Brownian limit $\gamma_\alpha = \sqrt{(m_0/m_\alpha)} \ll 1$ we decompose L_0^α and δL^α as was done in Section IV (see Eqs. (225), (226), (227), (228), (229), and (230)) and we expand $\square_{\mathbf{k}}^{\alpha}(z)$ in a series in γ_α:

$$\square_{\mathbf{k}}^{\alpha}(z) = \gamma_\alpha \square_{\mathbf{k}}^{\alpha(1)}(z) + \gamma_\alpha^2 \square_{\mathbf{k}}^{\alpha(2)}(z) + O(\gamma_\alpha^3) \tag{A.40}$$

where

$$\gamma_\alpha \square_{\mathbf{k}}^{\alpha(1)}(z) = -\int \prod_{i=1}^{N_0} d_i\mathbf{p} \left\langle \mathbf{k}_\alpha, \{0\} \left| \gamma_\alpha \delta L^{I,\alpha} \frac{1}{L^{f,\alpha} - z} (L_0^f - z) \right| \mathbf{k}_\alpha, \{0\} \right\rangle' \prod_{i=1}^{N_0} \phi_i^{\text{eq.}} \tag{A.41}$$

$$\gamma_\alpha^2 \square_{\mathbf{k}}^{\alpha(2)}(z) = \int \prod_{i=1}^{N_0} d\mathbf{p}_i \left\langle \mathbf{k}_\alpha, \{0\} \left| \gamma_\alpha \delta L^{I,\alpha} \frac{1}{L^{f,\alpha} - z} (\gamma_\alpha L_0^{I,\alpha} + \gamma_\alpha \delta L^{I,\alpha}) \right. \right.$$
$$\left. \left. \times \frac{1}{L^{f,\alpha} - z} (L_0^f - z) \right| \mathbf{k}_\alpha, \{0\} \right\rangle \prod_{i=1}^{N_0} \phi_i^{\text{eq.}} \tag{A.42}$$

For $z = i0$, it is easy to show that Eq. (A.41) reduces to:

$$\gamma_\alpha \square_{\mathbf{k}}^{\alpha(1)}(0) = \left\{ \int dr dv \sum_i \frac{\partial V^{0\alpha}}{\partial \mathbf{r}_i} \rho^{f,\alpha}(\mathbf{r}_i, \mathbf{v}_i) \right\} \frac{\partial}{\partial \mathbf{p}_\alpha} = 0 \tag{A.43}$$

which follows from a formula similar to Eq. (235) and from a symmetry argument, $\rho^{f,\alpha}$ being the equilibrium distribution of the fluid in the presence of the heavy particle fixed at $\mathbf{r}_\alpha$. Similarly one has:

$$\gamma_\alpha^2 \square_k^{\alpha(2)}(0) = \int dv \left\langle 0 | \{0\} | \gamma_\alpha \delta L^{I,\alpha} \frac{1}{L^f - i0} (\gamma_\alpha \delta L^{I,\alpha} + \gamma_\alpha L_0^{I,\alpha} \right.$$
$$\left. + \gamma_\alpha \mathbf{k}_\alpha \mathbf{v}_\alpha) \frac{L_0^f}{L^f - i0} \right| 0 \right\rangle \prod_i \phi_i^{\text{eq.}} \tag{A.44}$$

because, except for L_0^I, each operator involved in Eq. (A.42) is invariant in the change $\mathbf{k}_\alpha \to 0$. But we have:

$$\left\{ \int dv \left\langle 0, \{0\} \left| \gamma_\alpha \delta L^{I,\alpha} \left(\frac{1}{L^f - i0} \right)^2 \right| 0 \right\rangle \prod_i \phi_i^{\text{eq.}} \right\} \gamma_\alpha \mathbf{k}_\alpha \mathbf{v}_\alpha = 0 \tag{A.45}$$

again for symmetry reasons.

We thus have (Eqs. (233) and (304)):

$$i\gamma_\alpha^2 \square_{\mathbf{k}}^{\alpha(2)}(0) = i\gamma_\alpha^2 \square^{\alpha(2)}(0) \tag{A.46}$$

From Eqs. (A.43) and (A.46), Eq. (A.38) reduces to Eq. (385).

Appendix 3. Eigenvalues of the Inhomogeneous Fokker-Planck Operator

Let us consider the eigenvalue problem:

$$[-i\mathbf{k}\mathbf{v}_\alpha + i\Box^\alpha(0)]|\Psi_n^{\mathbf{k}}\rangle = \Lambda_n^{\mathbf{k}}|\Psi_n^{\mathbf{k}}\rangle \tag{A.47}$$

where the operator $i\Box^\alpha(0)$ has been defined in Eq. (304). First, we notice that for $\mathbf{k} = 0$, the solution of:

$$i\Box^\alpha(0)|\Psi_n^0\rangle = \Lambda_n^0|\Psi_n^0\rangle \tag{A.48}$$

is known.[19] Indeed in one dimension, we have, dropping the index α:

$$\frac{\zeta}{m}\frac{\partial}{\partial v}\left[v + \frac{kT}{m}\frac{\partial}{\partial v}\right]\Big|\Psi_n^{0_x}\rangle = \Lambda_{n^x}^{0_x}|\Psi_{n^x}^{0_x}\rangle \tag{A.49}$$

with

$$\Lambda_{n^x}^{0_x} = -n\frac{\zeta}{m}\ (n = 0, 1, 2\ .\ .\ .) \tag{A.50}$$

$$\langle v|\Psi_n^{0_x}\rangle = \exp\left(-\frac{mv^2}{2kT}\right)H_n\left(\frac{v\sqrt{m}}{\sqrt{2kT}}\right) \tag{A.51}$$

By separation of variables, we immediately obtain the eigenvalues and eigenfunctions of the three-dimensional problem (A.49).

Similarly, the solution of Eq. (A.47) is determined by the one-dimensional equation:

$$-ik_x v + \frac{\zeta}{m}\frac{\partial}{\partial v}\left[v + \frac{kT}{m}\frac{\partial}{\partial v}\right]|\Psi_{n^x}^{k_x}\rangle = \Lambda_{n^x}^{k_x}|\Psi_{n^x}^{k_x}\rangle \tag{A.52}$$

which we rewrite as:

$$\left(\frac{\partial^2}{\partial u^2} + u\frac{\partial}{\partial u} + 1 - iqu\right)|\Psi_{n^x}^{k_x}\rangle = \mu_{n^x}^{k_x}|\Psi_{n^x}^{k_x}\rangle \tag{A.53}$$

where we have introduced the dimensionless quantities:

$$u = v\sqrt{\frac{m}{kT}},\ q = k_x\frac{\sqrt{kTm}}{\zeta},\ \mu_n^{k_x} = \frac{m}{\zeta}\Lambda_n^{k_x} \tag{A.54}$$

This differential equation is easily transformed to the canonical equation of Hermite polynomials:

$$\frac{\partial^2}{\partial z^2} H_n(z) - 2z \frac{\partial}{\partial z} H_n(z) + 2nH_n(z) = 0 \tag{A.55}$$

by the transformation:

$$\langle u|\Psi_n^{k_x}\rangle = \exp\left[-\frac{(u+iq)^2}{2}\right] H_n\left(\frac{u+2iq}{\sqrt{2}}\right) \tag{A.56}$$

$$z = \frac{u+2iq}{\sqrt{2}}, \; n = \mu_n - q^2 \tag{A.57}$$

We deduce thus that:

$$\langle v|\Psi_n^{k_x}\rangle = \exp\left[-\frac{m}{2kT}\left(v + \frac{ik_x(kT)}{\zeta}\right)^2\right] \times H_n\left(\sqrt{\frac{m}{2kT}}\, v + \frac{ik_x\sqrt{2mkT}}{\zeta}\right) \tag{A.58}$$

while

$$\Lambda_n^{k_x} = -\frac{k_x^2(kT)}{\zeta} - \frac{n\zeta}{m} \tag{A.59}$$

Some care has to be exercised when demonstrating an expansion theorem in terms of Eq. (A.58), because the differential operator (A.52) is not Hermitian. It is, however, very easy to find a conjugate system of eigenfunctions:[24] they are obtained by substituting $-k_x$ for k_x in Eq. (A.58). We then have for an arbitrary function:

$$f(v_x) = \sum_n C_n \Psi_n^{k_x}(v_x) \tag{A.60}$$

where

$$C_n = \langle \Psi_n^{-k_x}|f\rangle = \left(\sqrt{2\pi}\, 2^n n!\, \sqrt{\frac{kT}{m}}\right)^{-1} \int dv_x \times \exp\left[\frac{mv_x^2}{2kT}\right] \exp\left[\frac{k_x^2 mkT}{\zeta^2}\right] \Psi_n^{k_x}(v_x) f(v_x) \tag{A.61}$$

With these results, we are now able to calculate the functions $\mathbf{J}_\nu'^B(\mathbf{k}; z)$, $P_\nu'^B(\mathbf{k}; z)$, $\mathbf{J}_\nu^B(\mathbf{k}; z)$, $\mathbf{H}_\nu^B(\mathbf{k}jz)$ and $\mathbf{L}_\nu^B(\mathbf{k}; z)$ defined respectively by Eqs. (387), (388), (399), (464), and (465). We shall

calculate explicitly one of these terms; for instance orienting $\mathbf{k}$ along v_{ν_x}, we have:

$$\mathbf{J}_\nu^B(\mathbf{k}; z) = Z_\nu \int \frac{1}{\mathbf{k}\mathbf{v}_\nu - \square^\nu - z} \frac{\partial}{\partial \mathbf{p}_\nu} \phi_\nu^{\text{eq.}} \, d^3p_\nu$$

$$= -iZ_\nu \sum_{\{n\}} \int \frac{1}{(-ikv_{\nu x} + i\square^\nu + iz)} \Psi^{k_x}_{\{n\}}(\mathbf{v}_\nu)$$

$$\times \left\langle \Psi^{-k_x}_{\{n\}} \right| \frac{\partial}{\partial \mathbf{p}_\nu} \phi_\nu^{\text{eq.}} \left\rangle d^3p_\nu \right. \tag{A.62}$$

where

$$|\Psi^{k_x}_{\{n\}}\rangle = |\Psi^{k_x}_{n_x} \Psi^0_{n_y} \Psi^0_{n_z}\rangle \tag{A.63}$$

If we limit ourselves to the case (see Eq. (396)):

$$k^2 \ll \zeta_\nu^2 / m_\nu kT \tag{A.64}$$

and take z at least of order

$$\zeta_\nu^2 / 2m_\nu kT \tag{A.65}$$

we get:

$$\mathbf{J}_\nu^B(\mathbf{k}; z) = Z_\nu \frac{1}{\left(\dfrac{-ik^2kT}{\zeta_\nu} - z\right)} \left\langle \Psi^{-k_x}_{\{0\}} \right| \frac{\partial}{\partial \mathbf{p}_\nu} \phi_\nu^{\text{eq.}} \left\rangle \int d\mathbf{p}_\nu \Psi^{k_x}_{\{0\}}(\mathbf{v}_\nu) \right. \tag{A.66}$$

Now from Eqs. (A.58) and (A.61), we get respectively:

$$\int d^3p_\nu \Psi^{k_x}_{\{0\}}(\mathbf{v}_\nu) = (2\pi kTm_\nu)^{3/2} \tag{A.67}$$

$$\left\langle \Psi^{-k_x}_{\{0\}} \right| \frac{\partial}{\partial \mathbf{p}_\nu} \phi_\nu^{\text{eq.}} \left\rangle = -\frac{1}{m_\nu(kT)} (2\pi kTm_\nu)^{-3} \int d^3v_\nu \exp\left(+\frac{m_\nu v_\nu^2}{2kT}\right) \right.$$

$$\times \exp\left(\frac{k^2 m_\nu kT}{\zeta_\nu^2}\right) \exp\left[-\frac{m_\nu}{2kT}\left(v_{\nu x} + \frac{ik\sqrt{kT}}{\zeta_\nu}\right)^2\right] v_{\nu x}$$

$$\times \exp\left(\frac{-m_\nu v_\nu^2}{2kT}\right) \tag{A.68}$$

This integral can be calculated immediately in the limit of small $\mathbf{k}$; we get, using condition (A.64):

$$\left\langle \Psi^{-k_x}_{\{0\}} \right| \frac{\partial}{\partial \mathbf{p}_\nu} \phi_\nu^{\text{eq.}} \left\rangle = \frac{i\mathbf{k}}{\zeta_\nu} (2\pi kT)^{-3/2} \right. \tag{A.69}$$

and the final expression for $J_\nu^B(\mathbf{k}; z)$ is thus:

$$\mathbf{J}_\nu^B(\mathbf{k}; z) = Z_\nu \frac{i\mathbf{k}}{\zeta_\nu \left(-\dfrac{ik^2(kT)}{\zeta_\nu} - z\right)} \tag{A.70}$$

which is precisely Eq. (391). The other integrals are calculated similarly; the only point worth noticing is that, to the order we consider, it is enough to calculate the tensor $\mathbf{L}_\nu^B(k; z)$ directly in the limit $\mathbf{k} = 0$.

Appendix 4. The Transport Equation for $\phi^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i)$

We derive here Eq. (428) from Eq. (427). First, in order to avoid any ambiguity in the limit $z = i0$, we set:

$$\Phi^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \lim_{z=i0} \Phi^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i; z) \tag{A.71}$$

where:

$$\Phi^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i; z) = \int \prod_{j\neq i} d\mathbf{p}_j \sum_{k'} \left\langle \mathbf{k}_\alpha, -\mathbf{k}_i \left| \frac{1}{L^{f,\alpha} - z} \right| k' \right\rangle (-i\mathbf{F}^\alpha \rho^{f,\alpha})_{k'}$$

We then expand the resolvant operator $(L^{f,\alpha} - z)^{-1}$ according to Eq. (35) and we get:

$$\Phi^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i; z) = \int \prod_{j\neq i} d\mathbf{p}_j \sum_{k'} \left\langle \mathbf{k}_\alpha, -\mathbf{k}_i \left| \sum_{n=0}^{\infty} \frac{1}{L_0 - z} \left(-\lambda\delta L^\alpha \frac{1}{L_0 - z} \right)^n \right| k' \right\rangle \times (-i\mathbf{F}^\alpha \rho^{f,\alpha})_{k'} \tag{A.73}$$

which we reclassify in terms of the irreducible collision operators Ψ and of the destruction operator $\tilde{\tilde{\mathscr{D}}}$, defined in Eqs. (429) and (430); we get thus the formal expansion:

$$\begin{aligned}
\phi^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i; z) = \int \prod_{l\neq i} d\mathbf{p}_l \sum_{k'} \Bigg\{ & \left\langle -\mathbf{k}_i \left| \frac{1}{L_0 - z} \right| -\mathbf{k}_i \right\rangle \\
& \times \tilde{\tilde{\mathscr{D}}}_{-\mathbf{k}_i,k'} (-i\mathbf{F}^\alpha \rho^{f,\alpha})_{k'} \\
& + \sum_{j \begin{cases} =i \\ \neq i \end{cases}} \left\langle -\mathbf{k}_i \left| \frac{1}{L_0 - z} \right| -\mathbf{k}_i \right\rangle \langle -\mathbf{k}_i | \Psi(z) | -\mathbf{k}_j \rangle \\
& \times \left\langle -\mathbf{k}_j \left| \frac{1}{L_0 - z} \right| -\mathbf{k}_j \right\rangle \tilde{\tilde{\mathscr{D}}}_{-\mathbf{k}j,k'} \\
& \times (-i\mathbf{F}^\alpha \rho^{f,\alpha})_{k'} + \cdots \Bigg\}
\end{aligned} \tag{A.74}$$

where the higher-order contributions are obtained by inserting more and more Ψ operators. In deriving Eq. (A.74), explicit account has been taken of the fact that all the terms involving the forces are included in the $\tilde{\tilde{\mathscr{D}}}$ term.

This equation is readily transformed to an integral equation for $\boldsymbol{\phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(z)$: one first remarks that the dummy particles (i.e. particles different from i and j in $\langle -\mathbf{k}_i|\Psi(z|\ -\mathbf{k}_j)\rangle$ never appear in two successive collision operators because otherwise we would get a negligible contribution in the limit of an infinite system:* moreover as these dummy particles have zero wave vectors in the initial state, they have a Maxwellian distribution of velocities (see Eq. (418)). This allows us to write Eq. (A.74) in the compact form:

$$\boldsymbol{\phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i;z) = \int \prod_{l\neq i} d\mathbf{p}_l \Bigg[\left\langle -\mathbf{k}_i \left| \frac{1}{L_0 - z} \right| -\mathbf{k}_i \right\rangle \sum_{k'} \tilde{\tilde{\mathscr{D}}}^{(\alpha i)}_{\mathbf{k}_i,k'} \times (-i\mathbf{F}^{\alpha}\rho^{f,\alpha})_{k'} + \sum_{n\begin{cases}\neq i\\ =i\end{cases}} \left\langle -\mathbf{k}_i \left| \frac{1}{L_0 - z} \right| -\mathbf{k}_i \right\rangle \langle -\mathbf{k}_i|\Psi(z)|-\mathbf{k}_n\rangle \times \boldsymbol{\phi}^{(\alpha n)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_n;z) \prod_{l\neq n} \phi_l^{\mathrm{eq.}} \Bigg] \tag{A.75}$$

Multiplying on both sides by $(-\mathbf{k}\mathbf{v}_i - z)$, we get:

$$(-\mathbf{k}\mathbf{v}_i - z)\boldsymbol{\phi}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i;z) - \int \prod_{j\neq i} d\mathbf{p}_j \sum_{k'} \tilde{\tilde{\mathscr{D}}}^{(\alpha i)}_{-\mathbf{k}_i;k'} (-i\mathbf{F}^{\alpha}\rho^{f,\alpha})_{k'} = \int \prod_{j\neq i} d\mathbf{p}_j \sum_{n\begin{cases}=i\\ \neq i\end{cases}} \langle -\mathbf{k}_i|\Psi(z)|-\mathbf{k}_n\rangle \boldsymbol{\phi}^{(\alpha n)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_n;z) \prod_{l\neq n} \phi_l^{\mathrm{eq.}} \tag{A.76}$$

We may now go to the limit $z \to i0$, in which case we recover Eq. (428).

Appendix 5. Small-Wave-Number Limit of the Effective Force $\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i)$

Equation (456), together with Eq. (457), may seem surprising at first sight because the lowest-order approximation ($\sim\lambda$) for

* It is easy to verify this statement on a simple example (see Résibois, and Davis,[32] Appendix I, for a similar situation).

$\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i)$ is simply (see the definition (455)):

$$\lambda\mathscr{F}^{(\alpha i)(1)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \lambda\langle 0|\mathbf{F}^{(\alpha i)}|\mathbf{k}_\alpha, -\mathbf{k}_i\rangle = -\frac{i\lambda}{\Omega}\,\mathbf{k}V^{(\alpha i)}_k \tag{A.77}$$

which tends to zero in the limit $\mathbf{k}\to 0$ provided V_0 exists, which we shall of course assume (we consider a short-range and non-singular potential).

We are, however, interested in the case of a strongly coupled system and it is not difficult to find another type of contribution, already of order λ^3. We may, for instance, consider the graph of

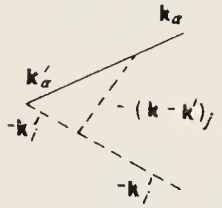

Fig. A.2. A simple example where $\lim_{k\to 0}\mathscr{F}^{(\alpha i)}_{\mathbf{k},-\mathbf{k}}$ is finite.

Fig. A.2. We have for this graph, according to Eq. (455):

$$\begin{aligned}\lambda^3\mathscr{F}^{\alpha i(3)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \lambda^3\int d\mathbf{p}_j \sum_j\sum_{k'}\langle 0|\mathbf{F}^{(\alpha i)}|\mathbf{k}'_\alpha - \mathbf{k}'_i\rangle\,\frac{1}{-\mathbf{k}'_i\mathbf{v}_i - i0}\\ \times\langle \mathbf{k}'_\alpha, -\mathbf{k}'_i|\delta L^{ij}|\mathbf{k}'_\alpha, -\mathbf{k}_i, (\mathbf{k}-\mathbf{k}')_j\rangle\\ \times\frac{1}{-\mathbf{k}_i\mathbf{v}_i + (\mathbf{k}-\mathbf{k}')_j\mathbf{v}_j - i0}\\ \times\langle \mathbf{k}'_\alpha, -\mathbf{k}'_i,(\mathbf{k}-\mathbf{k}')_j|\delta L^\alpha|\mathbf{k}^j_\alpha, -\mathbf{k}_i\rangle\phi^{\mathrm{eq.}}_j\end{aligned} \tag{A.78}$$

which may be explicitly written as:

$$\begin{aligned}\lambda^3\mathscr{F}^{(\alpha i)(3)}_{\mathbf{k},-\mathbf{k}}(\mathbf{p}_i) = \frac{i\lambda^3 C}{\Omega}\,\frac{1}{8\pi^3}\int d\mathbf{k}'\int d\mathbf{p}_j\\ \times\mathbf{k}'V^{(\alpha i)}_{\mathbf{k}'}\,\frac{1}{-\mathbf{k}'\mathbf{v}_i - i0}\,(\mathbf{k}-\mathbf{k}')V^{(ij)}_{|\mathbf{k}-\mathbf{k}'|}\,\frac{\partial}{\partial\mathbf{p}_i}\\ \times\frac{1}{-\mathbf{k}_i\mathbf{v}_i + (\mathbf{k}-\mathbf{k}')\mathbf{v}_j - i0}\,(\mathbf{k}-\mathbf{k}')V^{(\alpha j)}_{|\mathbf{k}-\mathbf{k}'|}\,\frac{\partial}{\partial\mathbf{p}_j}\,\phi^{\mathrm{eq.}}_j\end{aligned} \tag{A.79}$$

Instead of considering this integral for arbitrary $\mathbf{k}$, we shall simply show that the limit $\mathbf{k} = 0$ exists and is finite:

$$\lambda^3 \mathscr{F}_{0,0}^{(\alpha i)(3)}(p_i) = \frac{i\lambda^3 C}{\Omega} \frac{1}{8\pi^3} \int d\mathbf{k}' \int d\mathbf{p}_j \mathbf{k}' V_{k'}^{(\alpha i)} \frac{1}{-\mathbf{k}'\mathbf{v}_i - i0} \mathbf{k}' \times V_{\mathbf{k}'}^{(ij)} \frac{\partial}{\partial \mathbf{p}_i} \frac{1}{-\mathbf{k}'\mathbf{v}_j - i0} \mathbf{k}' V_{\mathbf{k}'}^{(\alpha j)} \frac{\partial}{\partial \mathbf{p}_j} \phi_j^{\text{eq.}} \tag{A.80}$$

$$= \frac{i\lambda^3 C}{\Omega} \frac{1}{8\pi^3} \frac{1}{kT} \left[\int d\mathbf{k}' V_{k'}^{(\alpha i)} V_{k'}^{(ij)} V_{k'}^{(\alpha j)} \times \frac{1}{\mathbf{k}'\mathbf{v}_i + i0} (\mathbf{k}' : \mathbf{k}') \right] \frac{\partial}{\partial \mathbf{p}_i} \tag{A.81}$$

where the tensorial character of the bracketed integral has been made explicit; the integration over the angles of $\mathbf{k}'$ is readily performed:

$$\int d\mathbf{k}' \mathbf{V}_{\mathbf{k}'}^{(\alpha i)} V_{\mathbf{k}'}^{(ij)} V_{\mathbf{k}'}^{(\alpha j)} \frac{1}{\mathbf{k}'\mathbf{v}_i + i0} (\mathbf{k}' : \mathbf{k}') = \frac{1}{v_i} \left[\int_0^\infty k'^3 dk' \times V_{\mathbf{k}'}^{(\alpha i)} V_{\mathbf{k}'}^{(ij)} V_{\mathbf{k}'}^{(\alpha j)} \right] \left[\mathbf{U} - 1_{v_i} : 1_{v_i} \right] \tag{A.82}$$

which is indeed of the type indicated in the second term of the r.h.s. of Eq. (456) and is finite provided all the V_k are well behaved.

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NUCLEAR PARAMAGNETIC RELAXATION IN SOLIDS

J. PHILIPPOT, University of Brussels, Brussels, Belgium

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I. INTRODUCTION

In this article, we study some aspects of irreversible processes in spins systems. We essentially treat nuclear paramagnetic relaxation; the case of ferromagnetism is not discussed.

After the pioneering work of Waller,[1] Casimir and Du Pré,[2] and Kronig and Bouwkamp,[3] the concept of spin temperature was justified by Abragam and Proctor.[4] Many authors[5–12] have been interested in the establishment of a Pauli equation, or in the study of the relaxation function in the limit of a high external magnetic field H_0 and of a high temperature (i.e. $H_l/H_0 \ll 1$, $\hbar\omega_0/kT \ll 1$, H_l being the local field and $\omega_0/2\pi$ the Larmor frequency in the field H_0). Significant progress was made recently by Anderson and Hartmann who introduced the notion of dipole–dipole temperature.

As an introduction to the peculiar properties of the spin Hamiltonians, we first give a short summary of the theory of spin relaxation in liquids where the problem is in fact a Brownian motion one. Then we consider the many-spin problem in solids and apply the general formalism of the theory of irreversible processes developed by Prigogine and his co-workers. We also analyse some aspects of the recent work of Caspers and Tjon on this subject. Finally, we indicate the special interest of spin–spin relaxation phenomena in connection with non-Markovian processes.

II. BROWNIAN MOTION PROBLEMS

A. Bloch Equations and the Phenomenological Point of View

In paramagnetic resonance experiments, the sample is usually placed in a large constant magnetic field $\mathbf{H}_0$, whose direction is taken as that of the z axis. This field determines the quantum levels of the individual spins and polarizes them according to Curie's law. In a typical nuclear resonance experiment, a radio-frequency field $\mathbf{H}_1$, perpendicular to $\mathbf{H}_0$ and rotating in the x,y plane is applied to the sample. The response of the system is, under stationary conditions, described by the radiofrequency susceptibility $\chi(\omega)$. The rotating field is given by

$$\mathbf{H}_1 = H_1(\cos \omega t\, \mathbf{1}_x + \sin \omega t\, \mathbf{1}_y) \tag{1}$$

and is considered as the properly rotating component of the oscillating field

$$H_x = 2H_1 \cos \omega t = 2\mathrm{Re}H_1 e^{i\omega t}$$

Then

$$\begin{aligned} M_x &= 2\mathrm{Re}\chi H e^{i\omega t} \\ &= \chi' 2H_1 \cos \omega t + \chi'' 2H_1 \sin \omega t \end{aligned} \tag{2}$$

where $\chi = \chi' - i\chi''$ is the complex susceptibility. χ' determines the component of the magnetic moment in phase with the field, whereas the out-of-phase component is proportional to χ''. This last quantity describes the absorption of electromagnetic energy by the spin system.

If all the magnetic moments $\boldsymbol{\mu}_k$ were independent, their equations of motion in the field $\mathbf{H}_0$ would be

$$d\boldsymbol{\mu}_k/dt = \gamma \boldsymbol{\mu}_k \times \mathbf{H}_0 \tag{3}$$

γ being the magnetogyric ratio of the spins, which, for simplicity, we assume to be all identical. In the absence of interaction among the spins, the resultant macroscopic magnetic moment **M** evolves according to the same equation

$$d\mathbf{M}/dt = \gamma \mathbf{M} \times \mathbf{H}_0 \tag{4}$$

The solution of this equation is a precession of the vector **M** around $\mathbf{H}_0$ with an angular velocity $\omega_0 = -\gamma \mathbf{H}_0$. It is clear that this equation does not describe how the magnetization reaches its equilibrium value. In order to explain how the spins approach their equilibrium distribution we must take account of the interactions of the spins among themselves and with the other degrees of freedom of the system. The simplest phenomenological description of the approach to equilibrium of an assembly of magnetic moments, placed in a constant field $\mathbf{H}_0$, is given by the equations

$$\frac{dM_z}{dt} = -\frac{(M_z - M_0)}{T_1}, \quad \frac{dM_x}{dt} = \frac{-M_x}{T_2}, \quad \frac{dM_y}{dt} = \frac{-M_y}{T_2} \tag{5}$$

where T_1 is the longitudinal relaxation time and T_2 the transversal relaxation time. To describe the behaviour of the system under the combined effect of the external field **H** and the interactions, Bloch[13] has written the following phenomenological equations

$$\begin{aligned}
\frac{dM_x}{dt} &= \gamma(\mathbf{M} \times \mathbf{H})_x - \frac{M_x}{T_2} \\
\frac{dM_y}{dt} &= \gamma(\mathbf{M} \times \mathbf{H})_y - \frac{M_y}{T_2} \\
\frac{dM_z}{dt} &= \gamma(\mathbf{M} \times \mathbf{H})_z - \frac{M_z - M_0}{T_1}
\end{aligned} \tag{6}$$

These equations, obtained by a simple superposition of the external force term and the relaxation term, give a quantitative agreement with experiment in the case of liquids. The stationary solution of Eq. (6) allows the calculation of χ.

B. The Stochastic Approach

If the interactions between the spins, or between the spins of different small groups considered as a whole, are weak compared

with the interactions with the other degrees of freedom of the system (usually called "the lattice"), spin relaxation is a typical Brownian motion problem. Each nucleus is submitted to the external field $\mathbf{H}_0$ and to a local fluctuating field $\mathbf{H}_l$. The local field comes from the other spins and is modulated by the time-dependent coordinates of the lattice, or from a coupling with other time-dependent degrees of freedom. For instance, nuclei with a quadrupole moment are coupled to the lattice coordinates through the gradient of the electric field. We may then consider that each spin relaxes independently and so have a Brownian motion problem where a few coordinates are coupled to a heat bath and Eqs. (6) are expected to hold. This occurs in the case of liquids. A stochastic treatment of this problem was first given by Bloembergen, Purcell, and Pound.[14] It was later generalized by Redfield.[15] These authors consider an ensemble of identical systems, each consisting of a single or a small group of spins. Each system has a Hamiltonian

$$\mathscr{H} = \mathscr{H}_0 + G(t) \tag{7}$$

The unperturbed Hamiltonian $\mathscr{H}_0$ is the same for all systems and is time-independent. The time-dependent perturbation $G(t)$, different for each system, is considered as a stationary stochastic variable. We may, without loss of generality, suppose that the mean value of $G(t)$ over the ensemble is equal to zero. We denote by $\alpha,\beta,\gamma, \ldots$ the eigenstates of $\mathscr{H}_0$, supposed to be non-degenerate, and by $\hbar\alpha, \hbar\beta, \ldots$ the corresponding energies. The correlation function is defined by

$$P_{\alpha\beta\alpha'\beta'}(\tau) = \overline{G_{\alpha\beta}(t)G_{\alpha'\beta'}(t-\tau)} \tag{8}$$

where $G_{\alpha\beta}(t) = \langle\alpha|G(t)|\beta\rangle$. The correlation time τ_c is such that $P(\tau) \ll P(0)$ for $\tau \gg \tau_c$. To establish an irreversible equation for the density matrix of the ensemble, $\bar{\bar{\sigma}}$, we start from the equation of motion of the density matrix, σ, of a single system

$$i\hbar \frac{d\sigma}{dt} = [\mathscr{H}_0 + G(t), \sigma] \tag{9}$$

We write its formal solution, take the mean over the ensemble,

and find in the long time–weak coupling approximation the equations

$$\frac{d}{dt}\bar{\bar{\sigma}}_{\alpha\alpha'} = -\bar{\bar{\sigma}}_{\alpha\alpha'}\left[\sum_{\gamma'}\right] J_{\gamma\alpha\gamma\alpha}(\gamma-\alpha) + \left]J_{\gamma\alpha'\gamma\alpha'}(\gamma-\alpha')\right] + 2\sum_{\gamma}\bar{\bar{\sigma}}_{\gamma,\alpha'\alpha+\gamma}J_{\alpha\gamma\gamma\alpha'-\alpha+\gamma}(\alpha-\gamma) \quad (10)$$

where

$$J_{\alpha\alpha'\beta\beta'}(\omega) = \frac{1}{2}\int_{-\infty}^{\infty} d\tau\, e^{i\omega\tau}P_{\alpha\alpha'\beta\beta'}(\tau) \quad (11)$$

If $\alpha = \alpha'$ Eq. (10) reduces to

$$\frac{d}{dt}\bar{\bar{\sigma}}_{\alpha\alpha} = -\bar{\bar{\sigma}}_{\alpha\alpha}2\sum_{\gamma} J_{\gamma\alpha\gamma\alpha}(\gamma-\alpha) + 2\sum_{\gamma}\bar{\bar{\sigma}}_{\gamma\gamma}J_{\alpha\gamma\alpha\gamma}(\alpha-\gamma) \quad (12)$$

showing that the transition probabilities are the Fourier transforms of the correlation functions, i.e. the spectral densities. The theory has been applied by Bloembergen to calculate the spin lattice relaxation time of a water molecule. We summarize his method here; this will allow us to become familiar with the properties of the dipole–dipole interaction. The relaxation mechanism is the rotational modulation of the dipole–dipole interaction of the two protons. This interaction has the form

$$V(1,2) = \frac{\gamma^2\hbar^2}{r^3}\left[\mathbf{I}(1)\cdot\mathbf{I}(2) - \frac{3}{r^2}(\mathbf{I}(1)\cdot\mathbf{r})(\mathbf{I}(2)\cdot\mathbf{r})\right] \quad (13)$$

It is the classical interaction potential between two magnetic dipoles, $\gamma\hbar\mathbf{I}$. This expression may be decomposed into a series of terms

$$V(1,2) = \sum_{s=0,\pm1,\pm2} V^{(s)}(1,2)$$

The $V^{(s)}$ are characterized by their commutation rules with the z component of the total angular momentum

$$S_z = \hbar[I_z(1) + I_z(2)]$$

These commutation relations are

$$[S_z, V^{(s)}] = s\hbar V^{(s)} \quad (14)$$

They show, for instance, that $V^{(1)}$ is an operator which creates a Zeeman quantum. Expressed in polar coordinates

$$V^{(0)}(1,2) = A + B$$
$$= \frac{\gamma^2\hbar^2}{r^3}\left\{I_z(1)I_z(2)(1 - 3\cos^2\theta) + [I_+(1)I_-(2) + I_-(1)I_+(2)]\frac{(3\cos^2\theta - 1)}{4}\right\}$$
$$V^{\pm 1}(1,2) = \frac{\gamma^2\hbar^2}{r^3}\{-\tfrac{3}{2}\sin\theta\cos\theta\, e^{\mp i\phi}[I_z(1)I_\pm(2) + I_z(2)I_+(1)]\}$$
$$V^{\pm 2}(1,2) = \frac{\gamma^2\hbar^2}{r^3}\sin^2\theta\, e^{\mp 2i\phi}I_+(1)I_\pm(2) \qquad (15)$$

where θ,ψ are the polar angles between the vector $\mathbf{r}$ joining the two spins and the polar axis z. The first term of $V^{(0)}(1,2)$, the A term in Van Vleck's notation, is the analogue of the static part of the classical local field. The B, or flip-flop, term allows an inversion of the spins of the two protons and corresponds to the transition induced by the rotating component of the local field. The total Zeeman energy does not change in such transitions. Therefore they do not contribute to the spin–lattice relaxation. The $V^{(s)}$ terms on the other hand cause an energy exchange between the spins and the lattice and are responsible for the spin–lattice relaxation. To calculate this relaxation time, we note that any $V^{(s)}$ term may be written as a product

$$V^{(s)}(1,2) = F^{(s)}(t)O^{(s)}(1,2)$$

of a function $F^{(s)}(t)$ depending on the coordinates of the thermostat and a spin operator $O^{(s)}$. The thermostat is usually treated classically and the rotation of the molecule may be approximated by an equation for diffusion over a sphere of the form

$$\frac{\partial\psi}{\partial t}(\theta,\phi,t) = \frac{D}{a^2}\Delta_s\psi(\theta,\phi,t)$$

The diffusion coefficient is estimated using Stokes law, $D = kT/8\pi\eta a$, where η is the viscosity and a the radius of the rotating sphere. This rough model allows a calculation of the correlation function. It turns out that a Boltzmann distribution remains a Boltzmann distribution so that the system of equations (12)

reduces to a single differential equation for the spin temperature. The calculated relaxation time agrees reasonably with the experimental one.

C. The Wangsness–Bloch Equations

Wangsness and Bloch[16,17] were the first to give a quantum mechanical treatment of spin relaxation using the density matrix formalism. The system considered is a spin interacting with an external magnetic field (which we suppose here to be constant) and with a heat bath. The corresponding Hamiltonian is

$$\mathscr{H} = \hbar E + \hbar F + \hbar G \tag{16}$$

where $\hbar E$, $\hbar F$, $\hbar G$ are respectively the Zeeman, the heat bath, and the interaction Hamiltonians. The interaction representation of the density matrix is

$$\tilde{\rho} = e^{-i\omega_0 I_z t}\, e^{-iFt} \rho\, e^{i\omega_0 I_z t}\, e^{iFt} \tag{17}$$

Using the long time–weak coupling approximation and the hypothesis of random phases for the thermostat, Bloch and Wangsness find, after taking the trace over the heat bath, the following equations for the reduced density matrix $\tilde{\sigma}$:

$$\frac{d}{dt}\tilde{\sigma}_{m,m'} = -\sum_{\tau}(\Gamma^{\tau}_{mm} + \Gamma^{\tau}_{m'm'})\sigma_{m,m'} + \sum_{\tau} 2e^{-\hbar\omega_0/kT}\Gamma^{\tau}_{mm'}\sigma_{m+\tau,m'+\tau} \tag{18}$$

These equations are valid in the absence of degeneracy. Like Eqs. (10) they are characterized by the fact that elements with the same difference of indices $m - m'$ are coupled among themselves. Their equilibrium solution is a Boltzmann distribution.

III. THE MANY-SPIN PROBLEM IN NUCLEAR PARAMAGNETIC RELAXATION

A. Introduction

In solids, the coupling between the spins is much larger than their coupling with the lattice. The spin–lattice relaxation time is therefore very long (a few minutes) compared with the spin–spin relaxation time. It was soon realized that, to a first approximation, the evolution of many-spin systems towards equilibrium

involves two steps. In the first one, the spin system reaches an internal equilibrium state characterized by a spin temperature. In the second and longer step the spins behave as a thermodynamical system in contact with the heat bath of the lattice. We shall see later how this picture has recently been refined. Spin–spin relaxation was first studied by Waller,[1] in the absence of an external field. Casimir and Du Pré[2] made the hypothesis that the spins could be treated as a thermodynamical system. Kronig and Bouwkamp[3] calculated the spin–spin relaxation time in the case of a large external field. In their theory, each spin is submitted to the external field and to a local magnetic field originating from the neighbouring spins. This field varies from one spin to the other. A spin can only be reversed in a relaxation process at the points where the local field compensates the external field $\mathbf{H}_0$, so that the total energy remains constant. This requires the orientation of a large number of neighbouring spins and becomes therefore highly improbable in a large external field, i.e. when $H_0 \gg H_l$.

The notion of spin temperature, which was criticized in connection with discussions of the Overhauser effect, has been justified by Abragam and Proctor.[4] These authors performed the first "calorimetric" experiments with spin systems. Anderson and Hartmann[7] proposed that the state of an assembly of interacting spins be characterized by two temperatures, a Zeeman and a dipole–dipole temperature. These ideas are now supported by a series of experiments and Jeener[9] has shown how these two "temperatures" could be measured simultaneously. After a study of the equilibrium thermodynamical properties of an assembly of interacting spins, we shall apply the general formalism of the theory of irreversible processes to study the evolution towards equilibrium. Finally, we shall analyse some aspects of the recent work of Caspers[5] and Tjon[11] on this subject.

B. Equilibrium Properties

The Hamiltonian of a rigid lattice of interacting spins placed in a large magnetic field H_0 directed along z is

$$\mathscr{H} = \mathscr{H}_{\text{Zeeman}} + \mathscr{H}_{\text{interaction}} \tag{19}$$

The interaction Hamiltonian is decomposed into a sum of terms characterized by their commutation relations with S_z:

$$\mathscr{H}_{\text{int.}} = \sum_{s=0,\pm 1,\pm 2} V^{(s)}, \quad V^{(s)} = \tfrac{1}{2} \sum_{k \neq l} V^{(s)}(k, l) \tag{20}$$

As an example of an interaction we shall take the dipole–dipole one, but it is clear that the addition of an exchange term does not modify the general line of thought. We first choose a representation with which to work. There are several possibilities: the representation where the $I_z(j)$ operator is diagonal for all spins j, the representation where the Zeeman energy and $V^{(0)}$ are simultaneously diagonal, and the representation where the total Hamiltonian is diagonal. We are immediately faced with one of the particular difficulties of the problem. To calculate the transition probabilities with a time-dependent perturbation theory, we need an unperturbed Hamiltonian with a continuous spectrum. We are thus led to work with the representation defined by the common eigenvectors of $\mathscr{H}_Z$ and $V^{(0)}$:

$$\begin{aligned} \mathscr{H}_Z |M, n\rangle &= M\hbar\omega_0 |M, n\rangle \\ V^{(0)} |M, n\rangle &= E_{M,n} |M, n\rangle \end{aligned} \tag{21}$$

In Eq. (21) M is either an integer or a half integer and n stands for all the other quantum numbers needed to define the corresponding eigenstate. We do not know the eigenstates and the eigenvalues of $V^{(0)}$. We nevertheless go ahead using this representation. If the final expressions can be written as traces, they may be calculated in the representation where the $I_z(j)$ are diagonal, as was done by Van Vleck.

Anderson and Hartmann were the first to show that a series of experiments could be interpreted by supposing the system to be described by a quasi-stationary density matrix

$$\rho = c \exp\left(-\beta_Z \mathscr{H}_Z - \beta_D V^{(0)}\right) \tag{22}$$

That such a matrix describes a metastable state when $H_0 \gg H_l$ can easily be seen and will be discussed in the following section. Since β_Z is related to the mean magnetic moment and β_D to the mean dipole–dipole energy, this raises the question of the independence of these two invariants of the motion. It may be shown[10] by introducing the Fourier transforms of the $I_z(j)$

operators that $\mathcal{H}_Z = \hbar\omega_0 I_z$ is a collective coordinate and that it may be considered as independent of the other coordinates of the dipole–dipole system in the limit $\hbar\omega_0/kT \ll 1$, which is the usual situation in paramagnetism. To develop the statistical mechanics of a system with two invariants of the motion, we remark that the problem is similar to that of an assembly of a given number of particles. The total magnetic moment plays the role of the number of particles operator. Using the formulae of the grand canonical ensemble, the density matrix is

$$\rho_{M,n;M,n} = \exp(-q + \nu M - \beta E_{M,n}) \tag{23}$$

The mean angular moment (in units of $\hbar$) is $\bar{M} = \partial q/\partial_\nu$ and the mean dipole–dipole energy is $\bar{E}_D = -\partial q/\partial\beta$. In the limit of high temperatures we may expand the exponential and retain only the linear terms. ν and β may then be considered as the coefficients of the expansion of ρ in orthogonal operators, since $Tr(V^{(0)}M_z) = 0$. In this limiting case it then becomes evident that ν and β are independent. It is easily shown that the thermodynamical temperature, defined by

$$\left(\frac{\partial S}{\partial E_{\text{total}}}\right)_{\bar{M}} = \frac{\partial S}{\partial \bar{E}_D} = \frac{1}{T} = \frac{1}{T_D} \tag{24}$$

is the dipole–dipole temperature, whereas the "Zeeman temperature" defined by

$$\frac{\partial S}{\partial \bar{E}_Z} = \frac{1}{T_Z} = \frac{k\nu}{\hbar\omega_0} \tag{25}$$

is a measure of the mean magnetic moment and is thus more related to a chemical potential.

C. Cross Relaxation[18]

This formalism allows us to write easily the equilibrium conditions in the case of assemblies of several spin species. Let us consider for instance the case of two magnetic ingredients. The Hamiltonian is

$$\mathcal{H} = \mathcal{H}_Z(1) + \mathcal{H}_Z(2) + V^{(0)}(1) + V^{(0)}(2) + V^{(0)}(1, 2) + \ldots \tag{26}$$

We use the basis vectors defined by

$$[\mathscr{H}_Z(1) + \mathscr{H}_Z(2)]|M_1, M_2, n\rangle = \hbar(M_1\omega_1 + M_2\omega_2)|M_1, M_2, n\rangle$$
$$[V^{(0)}(1) + V^{(0)}(2) + V^{(0)}(1, 2)]|M_1, M_2, n\rangle$$
$$= E_{M_1,M_2,n}|M_1, M_2, n\rangle \quad (27)$$

This constitutes a system with three quasi-invariants: the two magnetic moments and the dipole–dipole energy. The corresponding density matrix is

$$\rho_{M_1,M_2,n;M_1,M_2,n} = \exp(-q + \nu_1 M_1 + \nu_2 M_2 - \beta E_{M_1,M_2,n}) \quad (28)$$

The mean angular momenta and the chemical potentials are respectively given by

$$\bar{M}_i = \frac{\partial q_i}{\partial \nu_i}, \quad \mu_i = \left(\frac{\partial \bar{E}_t}{\partial \bar{M}_i}\right)_s = -T\left(\frac{\partial S}{\partial \bar{M}_i}\right)_{E_t} \quad (29)$$

Let us suppose that there exists a linear combination of the Larmor frequencies such that $\alpha_1\omega_1 + \alpha_2\omega_2 \simeq \Delta\omega$ where the α_i are integers close to one and where $\Delta\omega$ is the line width. In this case the $V^{(s)}$ terms of the perturbation induce an exchange of quanta between the two Zeeman subsystems, the energy balance being taken up by the dipole–dipole subsystem. One of the quasi-invariants is thus destroyed but the combination $M_1/\alpha_1 - M_2/\alpha_2$ remains constant. As in chemical thermodynamics,[19] it is useful here to introduce a reaction coordinate ξ to characterize the state of the system; we then have the relations:

$$\bar{M}_1(t) = \bar{M}_1(0) + \alpha_1 d\xi$$
$$\bar{M}_2(t) = \bar{M}_2(0) + \alpha_2 d\xi$$
$$\frac{d\bar{M}_1}{\alpha_1} = \frac{d\bar{M}_2}{\alpha_2} = d\xi \quad (30)$$

At equilibrium the affinity of the reaction is equal to zero:

$$A = \alpha_1\mu_1 + \alpha_2\mu_2 = 0 \quad (31)$$

The equilibrium values of $\bar{M}_1$, $\bar{M}_2$, $\bar{E}_D$ are thus fixed by Eqs. (30) and (31) and the condition of conservation of the total energy

$$\bar{E}_D + \bar{M}_1\hbar\omega_1 + \bar{M}_2\hbar\omega_2 = \bar{E}_t \quad (32)$$

An alternative treatment of the same problem consists in writing the Zeeman Hamiltonian in the form

$$\mathscr{H}_Z = \frac{1}{2}\left[\frac{S_z(1)}{\alpha_1} + \frac{S_z(2)}{\alpha_2}\right](\alpha_1\omega_1 + \alpha_2\omega_2) + \frac{1}{2}\left[\frac{S_z(1)}{\alpha_1} - \frac{S_z(2)}{\alpha_2}\right](\alpha_1\omega_1 - \alpha_2\omega_2) \qquad (33)$$

$S_z(i)$ being the total angular momentum of the i spins. The linear combination $S_z(1)/\alpha_1 + S_z(2)/\alpha_2$ is now coupled to the dipole–dipole heat bath, whereas the difference $S_z(1)/\alpha_1 - S_z(2)/\alpha_2$ remains constant. It may be shown that the chemical equilibrium condition (31) is then equivalent to an equalization of the temperatures of the collective coordinate $S_z(1)/\alpha_1 + S_z(2)/\alpha_2$ and of the dipole–dipole heat bath.

Jeener[9] has shown how similar considerations, based on the maximization of entropy, can be used to describe the stationary state of a system in the presence of a permanent weak irradiation.

D. Evolution of the Many-Spin System towards Equilibrium

We now analyse the role of the $V^{(s\neq 0)}$ terms. They cause a shift of the levels of the unperturbed Hamiltonian $\mathscr{H}_Z + V^{(0)}$ and induce transitions between eigenstates which will bring the system to equilibrium. We may also say that the perturbation $V^{(s)}$ couples the collective Zeeman coordinate to the dipole–dipole system. It is in fact a Brownian motion problem with the peculiarity that the single collective coordinate carries more energy than the whole "dipole–dipole heat bath". We shall first apply the long-time approximation, i.e. we shall consider the collisions as instantaneous. It turns out that in the representation chosen the processes bringing the dipole–dipole system into internal equilibrium are of the fourth order in the perturbation. This will lead us to write a generalized Pauli equation describing how the dipole–dipole system reaches equilibrium and how thermal equilibrium is established between the Zeeman coordinate and the dipole–dipole heat bath. This generalized Pauli equation justifies our equilibrium considerations and fixes the region of validity of Casimir and Du Pré's hypothesis.

We start from the non-Markovian master equation for the diagonal elements of ρ:[20,21]

$$\partial_t\langle k|\rho(t)|k\rangle = \int_0^t d\tau \left\{ \sum_{m=2}^{\infty} \left(\frac{\lambda}{i\hbar}\right)^m \int_0^{\tau} d\tau_1 \cdots \int_0^{\tau_{m-3}} d\tau_{m-2} \right.$$
$$\left. \langle k|[V(\tau), [V(\tau_1), [\cdots [V(0), \rho^{\mathrm{d}}(t-\tau)]\cdots]|k\rangle_{\mathrm{d.i.}} \right\} \quad (34)$$

The Hamiltonian has been written $\mathscr{H} = \mathscr{H}_0 + \lambda V$, the $|k\rangle$ are the eigenstates of $\mathscr{H}_0$, and $V(t)$ is the interaction representation of the perturbation

$$V = \sum_{s\neq 0} V^{(s)}$$
$$V(t) = \exp\left(\frac{(i\mathscr{H}_0 t)}{\hbar}\right) V \exp\left(-\frac{i\mathscr{H}_0 t}{\hbar}\right) \quad (35)$$

The subscript d.i. indicates the dynamical irreducible part.[21] The superscript indicates the diagonal part. To evaluate the kernel of this integral equation in the limit of long times, we apply the usual asymptotic formula

$$\lim_{T\to\infty} \int d\omega \int_{-T}^{T} f(\omega)\, e^{i\omega t} dt = 2\pi \frac{T}{|T|} f(0) \quad (36)$$

This formula is valid as soon as $T \gg (\Delta\omega)^{-1}$, where $\Delta\omega$ is the interval over which $f(\omega)$ varies appreciably. This interval is here the line width and $(\Delta\omega)^{-1}$ plays the role of a collision time. We now analyse successively the various terms of the collision operator.

(a) The λ^2 terms are the usual ones of the time-proportional transition probabilities:

$$\frac{2\pi}{\hbar} |(\sum_{s\neq 0} V^{(s)})_{M,n;M',n'}|^2 \delta[E_{M,n} - E_{M',n'} + (M'-M)\hbar\omega_0]$$

They correspond to the transitions

$$|M, n\rangle \leftrightarrows |M \pm s, n'\rangle$$

with an energy exchange $s\hbar\omega_0$ between the Zeeman and the dipole–dipole systems.

(b) The λ^3 terms are not interesting because they describe the same kind of processes as in (a) and are of a higher order in λ.

(c) The λ^4 terms are of two types. The first type of term

describes the same processes as in (a) and we shall therefore neglect them. The second type of term corresponds to transitions $|M, n\rangle \rightleftarrows |M, n'\rangle$ taking place within the dipole–dipole system. In order to classify these terms we could use the diagram technique introduced by Fujita.[22] However, since we are interested in the case of a high field H_0 and since in that case there are no intermediate states conserving energy, we may simply take the square of the S matrix and obtain for the transition probabilities the expression

$$\frac{2\pi}{\hbar}\,\delta(E_{M,n} - E_{M,n'}) \times \Big|\sum_s \sum_{n''} \langle M, n'|V^{(s)}(E_{M,n} - E_{M-s,n''} - s\hbar\omega_0 + i\varepsilon)^{-1}V^{(s)}|M, n\rangle\Big|^2 \quad (37)$$

Using the formula

$$\lim_{\varepsilon\to 0} \frac{1}{x + i\varepsilon} = P\left(\frac{1}{x}\right) - i\pi\delta(x)$$

and dropping the δ term, we get

$$\frac{2\pi}{\hbar}\,\delta(E_{M,n} - E_{M,n'})\,\Big|\sum_s [V^{(s)}, V^{(-s)}]_{M,n;M,n'}(s\hbar\omega_0)^{-1}\Big|^2$$

The final result takes the form of a generalized Pauli equation:

$$\begin{aligned}\partial_t \rho_{M,n;M,n} = {} & \frac{2\pi}{\hbar}\sum_{n'}\Big|\Big(\sum_s V^{(s)}\Big)_{M,n;M',n'}\Big|^2 \\ & \times (\rho_{M',n';M',n'} - \rho_{M,n;M,n})\delta[(M' - M)\hbar\omega_0 + E_{M,n} - E_{M',n'}] \\ & + \frac{2\pi}{\hbar}\sum_{n'}\Big|\sum_s [V^{(s)}, V^{(-s)}]_{M,n;M,n'}(s\hbar\omega_0)^{-1}\Big|^2 \\ & \times (\rho_{M,n;M,n'} - \rho_{M,n;M,n})\delta(E_{M,n} - E_{M,n'}) \end{aligned} \quad (38)$$

In the absence of special phase correlations we neglect the contribution of the non-diagonal elements of ρ at the initial time because they always contain at least one factor λ more than the retain term. Equation (38) is valid when

$$\tau_{\text{collision}} \ll \tau_{\text{dipole–dipole}} \ll \tau_{\text{dipole–Zeeman}} \ll \tau_{\text{spin–lattice}}$$

This is the usual situation in a high field. It is characterized by the fact that transitions between different M bands of the spectrum are highly improbable because of the vanishingly small relevant density of states or because of the high number of spins that have to be rearranged in order to distribute a Zeeman quantum over

the degrees of freedom of the dipole–dipole system. On the other hand, the transitions between different states of the dipole–dipole system but within the same Zeeman band ($\Delta M = 0$) easily fulfil the condition of energy conservation, and although being of the order λ^4 occur much more rapidly than the λ^2 transitions. This is the reason why in the high-field situation we may decompose the evolution into two steps. In the first one, the dipole–dipole system reaches internal equilibrium. The equations describing this evolution are obtained by neglecting the λ^2 terms in Eqs. (38), which gives a set of separated equations for each M. In order to evaluate the characteristic dipole–dipole relaxation time, it is necessary to go from these equations to a Boltzmann-like equation. Unfortunately, this has not yet been done since we do not know the representation with which we are working. We expect this time to be of the order of $(\Delta\omega)^{-1}(H_0/H_l)^2$, and it would be most interesting to set up experiments in order to measure this time. However, it does not seem to be simply related to a macroscopic observable. Up until now, many experiments have been interpreted using variable Zeeman and dipole–dipole temperatures, but it has not yet been possible to see how the dipole–dipole system reaches a canonical distribution by following the Brownian motion of one of its coordinates. If we remember the expansion of ρ in orthogonal operators:

$$\rho = \alpha 1 + \beta \mathscr{H}_Z + \gamma V^{(0)} + \ldots \tag{39}$$

we note that the possibility of measuring $Tr(V^{(0)}\rho)$ does not imply that the dipole–dipole system has reached internal equilibrium.

The second step of the evolution towards equilibrium is the Zeeman dipole–dipole relaxation. Hartmann and Anderson estimated this time using the hypothesis that ρ at any time is of the form (22). As a consequence of the shortness of the dipole–dipole relaxation time we may assume that the dipole–dipole system always remains in equilibrium; we are thus led to treat the evolution of the Zeeman system as the Brownian motion of a collective coordinate in the dipole–dipole heat bath. We assume that the diagonal elements of ρ have the form

$$\begin{aligned} \rho_{M,n;M,n} &= \sigma_{M;M} \exp(-\beta_D E_n)/Tr_{(n)}1 \\ &= \sigma_{M;M} \exp(-\beta_D E_n)/g(M) \end{aligned} \tag{40}$$

with the normalization

$$\sum_{M,n} \rho_{M,n;M,n} = \sum_{M} \sigma_{M;M} = 1$$

Substituting in Eq. (38) and taking the trace over the variables of the dipole–dipole system, we get a set of equations analogous to the Bloch equations (18)

$$\partial_t \sigma_{M;M} = -\sum \{2\Gamma^{(s)}_{MM}[\sigma_{M;M} - \exp(-\beta_D s\hbar\omega_0)_{M+s;M+s} g(M)/ g(M+s)]\} \quad (41)$$

with

$$\Gamma^{(s)}_{MM} = \sum_{m,n'} V^{(s)}_{M,n;M+s,n'} V^{(s)}_{M+s,n';M,n} \exp(-\beta_D E_k) \times \frac{\pi}{\hbar g(M)} \delta(E_{M,n} - E_{M+s,n'} + s\hbar\omega_0) \quad (42)$$

In contrast with the usual Brownian motion problems the temperature of the thermostat does not remain constant but is determined by the conservation law

$$\frac{d}{dt} \mathrm{Tr}[\rho(\mathscr{H}_Z + V^{(0)})] = 0 \quad (43)$$

because the single Zeeman collective coordinate carries the largest part of the total energy. These equations may be simplified in the case of small deviations from equilibrium. Looking for a solution of the form

$$\sigma_{M,M}(t) = g(M) \exp[\beta_D(t) M\hbar\omega_0]/\mathrm{Tr}1 \quad (44)$$

we get

$$\frac{d}{dt}\beta_Z = \sum_s 2\Gamma^{(s)}_{MM} M^{-1}(\beta_D - \beta_Z) \quad (45)$$

Finally, assuming that the Γ_{MM} are slowly varying with M and that the relevant values of M are practically equal to $\bar{M}$, the set (45) is replaced by the equation

$$\frac{d}{dt}\beta_Z = \sum_s \mathrm{Tr}[V^{(s)} V^{(-s)} \pi\hbar\delta(E_{M,n} - E_{M+s,n'} + s\hbar\omega_0)] \times (\beta_D - \beta_Z)/\mathrm{Tr}S_z^2 \quad (46)$$

This is the result of Hartmann, Anderson, and Provotoroff.

E. Caspers' Theory[5]

Caspers has developed a theory of spin–spin relaxation starting from the general expressions established by Kubo and Tomita.[23] His results however differ from those of Hartmann and Anderson and have been criticized recently by Tjon.[11] We shall first outline the main points of Caspers' method and then examine the basis on which it may be criticized.

When a sample is submitted to a constant external field $\mathbf{H}_0 + \mathbf{h}$ directed along the z axis and the small field $\mathbf{h}$ is suddenly switched off at $t = 0$, the linear response of the system is given by

$$\bar{M}_z(t) - \bar{M}_z^{(t)} = \phi_{zz}(t)h \tag{47}$$

where $\bar{M}_z(t)$ is the average magnetic moment at time t and $\bar{M}_z^{(0)}$ is the equilibrium magnetization in the presence of the external field $\mathbf{H}_0$ alone. The system which is in equilibrium in a field $\mathbf{H}_0 + \mathbf{h}$ for $t < 0$ is described by a canonical density matrix

$$\rho(t < 0) = \exp\{-\beta[(H_0 + h)M_z + \sum_s V^{(s)}]\}/\mathrm{Tr}\{\ldots\} \tag{48}$$

Retaining only the first terms of the expansion in $\hbar\omega/kT$, we find for the function $\phi_{zz}(t)$, which is still an extensive quantity, the expression

$$\phi_{zz}(t) = \beta \mathrm{Tr}[M_z M_z(t)](\mathrm{Tr}1)^{-1} \tag{49}$$

where $M_z(t)$ is M_z in the Heisenberg representation. To evaluate this expression, Caspers uses a representation in which the total Hamiltonian is diagonal. He splits the trace into the sum of the diagonal elements which is time-independent and the sum of the non-diagonal elements:

$$\mathrm{Tr}[M_z M_z(t)] = \sum_n |\langle n|M_z|n\rangle|^2 + \sum_{n \neq m} \langle n|M_z|m\rangle\langle m|M_z(t)|n\rangle \tag{50}$$

or, dividing by $N\mathrm{Tr}1 = Np$, in order to obtain an intensive quantity:

$$N^{-1}\langle\langle M_z M_z(t)\rangle\rangle = \sum_n |\langle n|M_z|n\rangle|^2 (pN)^{-1} + \Omega(t) \tag{51}$$

where the double brackets $\langle\langle\ \rangle\rangle$ denote the normalized trace.

The elements $\langle m|M_z(t)|n\rangle$ appearing in $\Omega(t)$ are then expressed by means of the formal solution

$$M_z(t) = M_z + \sum_{l=1}^{\infty} (i\hbar)^{-l} \int_0^t dt_l \int_0^{t_l} dt_{l-1} \cdots \int_0^{t_2} dt_1 \, [M_z;\ V(t_1), V(t_2), \ldots V(t_l)] \quad (52)$$

where $V = \sum_{s=\pm 1,\pm 2} V^{(s)}$, $V(t)$ is V in the interaction representation, and the notation $[;\ ,\ \ldots]$ stands for the commutator of the commutators. One then finds for $\Omega(t)$ the expression

$$\Omega(r) = \sum_{l=0}^{\infty} \Omega_l(t)$$

$$\Omega_l(t) = \lim_{N\to\infty} (i\hbar)^{-l} \int_0^t dt_1 \int_0^{t_1} dt_2 \cdots \int_0^{t_{l-1}} dt_l \, (pN)^{-1} \times \sum_{n\neq m} \sum_{\{s_i\}}{}' \langle n|M_z|m\rangle\langle m|[M_z;\ V^{(s_1)}(t_1), V^{(s_2)}(t_2), \ldots]|n\rangle \quad (53)$$

where $\sum'$ indicates that $\sum_i s_i = 0$ and $s_i \neq 0$. The commutators are then written in terms of irreducible tensors or developed in orthogonal operators, one of them being precisely M_z:

$$(i\hbar^{-l} \sum_{\{s_i\}}{}' [M_z;\ V^{(s_1)}(t_1), \ldots V^{(s_l)}(t_l)] = -g_l M_z^2 + \ldots$$

with

$$g_l(t_1 - t_2, t_2 - t_3, \ldots, t_{l-1} - t_l) = \mathrm{Tr}\{\sum_{\{s_i\}}{}' [M_z;\ V^{(s_1)}(t_1), \ldots, V^{(s_l)}(t_l)] M_z\}(i\hbar)^{-l}[\mathrm{Tr}(M_z^2)]^{-1} \quad (54)$$

In general, the g_l contain a sum of products of g_k with $k < n$, which can be found by means of repeated reductions of lower order. That part of $-g_l M_z$ which cannot be reduced to an expression in terms of g_k with a lower index is called by Caspers the irreducible principal diagonal part and is written

$$-h_l(t_1 - t_2, t_2 - t_3, \ldots, t_{l-1} - t_l) M_z$$

The functions g_l can be decomposed into a sum of terms characterized by the number of time arguments on which they depend:

$$\begin{aligned} g_l(t_1 - t_2, \ldots, t_{l-1} - t_l) &= h_l(t_1 - t_2, \ldots, t_{l-1} - t_l) \\ &- \sum_{q=2}^{l-2} h_q(t_1 - t_2, \ldots, t_{q-1} - t_q) h_{l-q}(t_{q+1} - t_{q+2}, \ldots, t_{l-1} - t_l) \\ &+ \sum_{q=2}^{l-4} \sum_{r=2}^{l-q-2} h_q(t_1 - t_2, \ldots, t_{q-1} - t_q) h_r(t_{q+1} - t_{q+2}, \ldots, t_{q+r-1} \\ &- t_{q+r}) \times h_{l-q-r}(t_{q+r+1} - t_{q+r+2}, \ldots, t_{l-1} - t_l) - \ldots \end{aligned} \tag{55}$$

The reduced form of the l-th commutator is then

$$\begin{aligned} &(i\hbar)^{-l} \sum_{\{s_i\}} [M_z;\ V^{(s_1)}(t_1), \ldots, V^{(s_l)}(t_l)] \\ &= - M_z[h_l(t_1 - t_2, \ldots, t_{l-1} - t_l) \\ &- \sum_{q=2}^{l-2} h_q(t_1 - t_2, \ldots, t_{q-1} - t_q) h_{l-q}(t_{q+1} - t_{q+2}, \ldots, t_{l-1} - t_l) \\ &+ \sum_{q=2}^{l-4} \sum_{r=2}^{l-q-2} h_q(t_1 - t_2, \ldots, t_{q-1} - t_q) h_r \\ &\times (t_{q+1} - t_{q+2}, \ldots, t_{q+r-1} - t_{q+r}) \\ &\times h_{l-q-r}(t_{q+r+1} - t_{q+r+2}, \ldots, t_{l-1} - t_l) + \ldots] \\ &+ T_l(t_1, t_2, \ldots, t_l) \end{aligned} \tag{56}$$

The last term T_l is the rest of the development, involving all the orthogonal operators, with the exclusion of M_z. Caspers assumes that the contribution of the terms which are not principal diagonal may be neglected in the case of large fields. He then finds that for large H and t, Ω fulfils the integral equation

$$\begin{aligned} \frac{d\Omega}{dt} = - \int_0^t dt_1 h_2(t_1) \Omega(t - t_1) - \int_0^t \int_0^{t-t_1} dt_2 h_3(t_1, t_2) \\ \times \Omega(t - t_1 - t_2) - \ldots \end{aligned} \tag{57}$$

This equation has the asymptotic solution $\Omega(t) \simeq A \exp(-/\tau)$, where the relaxation time is given by the series $1/\tau = \sum_{l=1}^{\infty} 1/\tau_l$

$$\frac{1}{\tau_1} = \int_0^\infty dt_1 h_2(t_1), \quad \frac{1}{\tau_2} = \int_0^\infty dt_1 \int_0^\infty dt_2 h_3(t_1 - t_2), \ldots \tag{58}$$

and

$$\tau_1 = \frac{\langle\langle M_z^2 \rangle\rangle}{\int_0^\infty d\tau \langle\langle [M_z, V(\tau)], V] M_z \rangle\rangle} \tag{59}$$

The time dependence of the principal diagonal part $-h_l M_z$ indicates that this term corresponds to the one which is selected by the condition of dynamic irreducibility in Prigogine and Résibois's formalism. However, it is for the complete expression $\mathrm{Tr}[M_z M_z(t)]$ that one is allowed to retain in the development of $M_z(t)$ only the part proportional to M_z and not for $\Omega(t)$.

In order to calculate $d\ \mathrm{Tr}[M_z M_z(t)]/dt$ we start from the integral equation which we may directly write down for the diagonal elements of $M_z(t)$ in the representation in which $\mathscr{H}_0$ is diagonal:

$$\frac{d}{dt}(M_z^{\mathrm{d}}(t)) = \int_0^t d\tau \sum_{m=2}^{\infty} (-i\hbar)^{-m} \int_0^\tau d\tau_1 \ldots \int_0^{\tau_{m-3}} d\tau_{m-2}$$
$$[V(\tau), V(\tau_1), \ldots, V(\tau_{m-2}), V(0);\ M_z^d(t-\tau)]_{\mathrm{d.i.}} \tag{60}$$

In the limit of instantaneous collisions ($t \gg (\Delta\omega)^{-1}$) this equation reduces to

$$\frac{d}{dt} M_z(t)_{k,k} = -M_z(t)_{kk} \sum_l |V_{kl}|^2 \frac{2\pi}{\hbar} \delta(E_k - E_l)$$
$$+ \sum_l M_z(t)_{ll} |V_{kl}|^2 \frac{2\pi}{\hbar} \delta(E_k - E_l) \tag{61}$$

which is analogous to the Pauli equation and where we have used the indices k,l to denote the eigenstates of $\mathscr{H}_0$. The time derivative of $\mathrm{Tr}[M_z M_z(t)]$ is then obtained directly from Eq. (61). For t goes to infinity, the diagonal elements of $M_z(t)$ tend to the constant $\langle M_z \rangle_E$ over the corresponding microcanonical surface of $\mathscr{H}_0$. It follows that $\langle\langle M_z M_z(t) \rangle\rangle$ tends to $\langle\langle \langle M_z \rangle_2^E \rangle\rangle$, in agreement with Tjon's theory (cf. Eq. (70)). We therefore believe that Caspers' equation (57) is not correct.

This integral equation for Ω reduces in the limit of instantaneous collisions ($t \gg (\Delta\omega)^{-1}$) to a closed differential equation for $1/TZ$:

$$\frac{d}{dt}\left(\frac{1}{T_Z} - \frac{1}{T_Z^0}\right) = -\frac{1}{\tau}\left(\frac{1}{T_Z} - \frac{1}{T_Z^0}\right) \tag{62}$$

To understand clearly the origin of the disagreement between Eq. (62) and Anderson and Hartmann's result, let us reformulate the problem in terms of the Zeeman temperature T_Z and the dipole–dipole temperature T_D. At time zero, the density matrix is

$$\rho(t \leqslant 0) = \exp\left[\frac{(H_0 + h)M_z}{kT_Z} - \frac{V^{(0)}}{kT_D}\right](\mathrm{Tr}1)^{-1}$$
$$= \exp\left[\frac{H_0 M_z}{kT'_z} - \frac{V^{(0)}}{kT_D}\right](\mathrm{Tr}1)^{-1} \tag{63}$$

with $H_0/kT'_Z = (H_0 + h)/kT_2$ and $T_Z = T_D$. The evolution towards equilibrium consists of an equalization of the two temperatures. The variation of $\bar{M}_z$ is given by the equation

$$\frac{d}{dt}\bar{M}_z = \mathrm{Tr}\left(\frac{d\rho}{dt}M_z\right)$$

which leads directly to Anderson and Hartmann's coupled equations

$$\frac{d}{dt}\left(\frac{1}{T_Z}\right) = \frac{1}{\tau_{12}}\left(\frac{1}{T_Z} - \frac{1}{T_D}\right)$$
$$\frac{d}{dt}\left(\frac{1}{T_D}\right) = \frac{1}{\tau_{21}}\left(\frac{1}{T_D} - \frac{1}{T_Z}\right) \tag{64}$$

It follows that the spin–spin relaxation time (exactly the Zeeman, dipole–dipole relaxation time) is not τ_{12} but

$$\tau_r = \frac{\frac{1}{2}H_{l_{\mathrm{sec}}}^2}{H^2 + \frac{1}{2}H_{l_{\mathrm{sec}}}^2}\tau_{12} \tag{65}$$

with

$$H_{l_{\mathrm{sec}}}^2 = \frac{2\mathrm{Tr}[V^{(0)}]^2 H^2}{\mathrm{Tr}\,\mathscr{H}_Z^2}$$

Caspers' relation τ of Eq. (62) is in fact equal to the τ_{12} of Eq. (64). But this author essentially looks for a closed equation for $\bar{M}_z$ without going into the details of the description of the energy exchange between the Zeeman coordinate and the dipole–dipole system. He therefore confuses τ_{12} with the spin–spin relaxation time.

F. Tjon's Theory

In connection with the separation (51) it is interesting to look at the corresponding expressions given by Tjon. The representation used is defined by

$$(\mathscr{H}_Z + V^{(0)})|E,M,\alpha\rangle = E|E,M,\alpha\rangle$$
$$S_z|E,M,\alpha\rangle = M\hbar|E,M,\alpha\rangle \quad (66)$$

and $M_z = \gamma S_z$. E is the total unperturbed energy and $M\hbar$ the angular momentum. It follows from the Pauli equation that

$$\lim_{t->\infty} \langle\langle M_z M_z(t)\rangle\rangle = (\mathrm{Tr}1)^{-1} \sum_E \rho_E \langle M_z\rangle_E^2 \quad (67)$$

where $\langle M_z\rangle_E$ is the microcanonical average of M_z with respect to the unperturbed Hamiltonian $\mathscr{H}_0$:

$$\langle M_z\rangle_E = \gamma\hbar \sum_M \frac{\rho_E(M)M}{\rho_E} \quad (68)$$

ρ_E being the number of microscopic states in the energy shell E

$$\rho_E = \sum_M \rho_E(M) \quad (69)$$

In the case of slight deviations from equilibrium, Tjon obtains the relation

$$\langle\langle M_z M_z(t)\rangle\rangle = \langle\langle \langle M_z\rangle_E^2\rangle\rangle + \{\langle\langle M_z^2\rangle\rangle - \langle\langle \langle M_z\rangle_E^2\rangle\rangle\} e^{-\Gamma t} \quad (70)$$

which should be compared with Eqs. (51) and (57). Equation (70) shows clearly that the equilibrium value of $\langle\langle M_z M_z(t)\rangle\rangle$ is $\langle\langle \langle M_z\rangle_E^2\rangle\rangle$. The quantity going exponentially to zero is the difference $\langle\langle M_z^2\rangle\rangle - \langle\langle \langle M_z\rangle_E^2\rangle\rangle$. This quantity is not equal to $\Omega(t)$.

Tjon has also written an integral equation for the diagonal elements of M_z, in the representation in which $\mathscr{H}_z + V^{(0)}$ is diagonal. He therefore assumes that the non-secular perturbation $V = \sum_{s\neq 0} V^{(s)}$ has matrix elements with randomly varying phases, and obtains the integral equation

$$\frac{d}{dt} M_z^{\mathrm{d}}(t) = -\int_0^t d\tau [[M_z^{\mathrm{d}}(t-\tau), V(\tau)], V(0)]^{\mathrm{d}} \quad (71)$$

for the diagonal part of $M_z(t)$. However, we think that the assumption of randomly varying phases of the matrix elements of V is

not justified unless the problem itself presents an element of randomness such as in the case of scattering by randomly distributed centres. This is the problem of the exact properties of Van Hove's δ singularity.[24] Moreover, even with this assumption we expect that the kernel will be of infinite order as in Eq. (60). In fact in Eq. (38) we have already met a kernel of the fourth order.

IV. NON-MARKOVIAN PROCESSES IN NUCLEAR PARAMAGNETIC RELAXATION

A. Introduction

Spin systems form particularly favourable material for the study of irreversible processes. They may be easily prepared in non-equilibrium states by methods such as adiabatic and sudden magnetization and demagnetization, impulse techniques, double frequency irradiation of systems with two kinds of nuclei, . . . A process going on in a low field may be stopped at any time by the sudden application of a high field, allowing a detailed analysis of the time evolution of the magnetization. The characteristic times are relatively long and one may easily follow the approach to equilibrium. The quantity playing the role of the collision time is $(\Delta\omega)^{-1}$, the inverse of the line width, which for interacting nuclear spins in solids is of the order of 10^{-4} sec. It is thus possible to observe the evolution for times smaller than the collision time. The usual asymptotic formula (36) used to set up a rate equation is not applicable and the phenomena are described by the non-Markovian equation (34). An oscillatory approach to equilibrium has been observed in several experiments concerning assemblies of nuclear spins in solids. Our main object is to understand the nature of these damped oscillations in the light of the general theory of irreversible processes.

B. The Free Precession Signal

We consider systems whose Hamiltonian may be split into an unperturbed term $\mathscr{H}_0$ with a continuous spectrum and a perturbation causing the evolution towards equilibrium. We shall first consider observables which do not commute with $\mathscr{H}_0$. A beautiful example of such a phenomenom is the free precession signal studied in detail by Lowe and Norberg.[25] Let us recall

briefly the essential features of the process.[26] One starts with a system initially in equilibrium in the constant magnetic field $\mathcal{H}_0$ directed along z. The sample is then submitted to a $\pi/2$ radio-frequency pulse. This brings the magnetic moment into the x,y plane. One then observes its rotation and the decay of its amplitude. The free precession signal $F(t)$ is the Fourier transform of the line shape $g(\omega)$. Therefore the function $F(t)$ does not obey any differential or integral equation unless $g(\omega)$ itself fulfils some particular property. One has here an example of a system showing some kind of memory. However, this effect is not described by the general non-Markovian equation of the theory of irreversible processes as supposed by Van Hove and Verboven.[27] The damping of the free precession signal is mainly due to the action of the unperturbed Hamiltonian $\mathcal{H}_Z + V^{(0)}$, where $\mathcal{H}_Z$ is the Zeeman Hamiltonian and $V^{(0)}$ the part of the spin–spin interaction which commutes with it. This kind of irreversible process, related to the uniformization in space of angular variables, is the most simple one, and was studied by Borel.[28] From a mathematical point of view, the irreversibility is a consequence of the vanishing of the Fourier transform of functions of class L_1, for $t \to \infty$.[29]

C. The Evolution of $\bar{M}_x$

The second group of quantities presenting damped oscillations is that of operators which do commute with the unperturbed Hamiltonian.[30] In the presence of a perturbation, the evolution of any diagonal element of the density matrix (i.e. diagonal in the representation where $\mathcal{H}_Z + V^{(0)}$ is diagonal) depends on the other diagonal elements and on the off-diagonal elements at the initial time. The influence of the off-diagonal elements taken at the initial time is described in Prigogine and Résibois's formalism by the "destruction term".[20,21] The two contributions are separated in the non-Markovian master equation for the diagonal part ρ^d of the density matrix:

$$\frac{\partial \rho^d}{\partial t} = \int_0^t K(\tau)\rho^d(t-\tau)d\tau + \text{destruction term} \qquad (72)$$

In the formulation of Zwanzig,[31] used by Provotoroff,[6] the density matrix (or the distribution function) is separated by

means of a projection operator into a "relevant part" and an "irrelevant part". The destruction term is the term depending on f_2 $(t = 0)$ in equation (11) of Zwanzig's article. Equation (72) shows how the correlations initially present in the system (represented by the off-diagonal elements of the density matrix) are destroyed while new correlations are built up from the diagonal elements. The destruction term plays a most important role in all the situations where the initial state shows special correlations.[32] Examples of these initial states are those which appear after submitting the system to impulses or after imagining a time inversion. The phenomena we shall discuss presently cannot be explained starting from the Pauli equation alone. In this theory it is supposed that off-diagonal elements have random phases and do not make any contribution to the evolution of the diagonal elements of ρ. In contrast with what happens with the Pauli equation, where the solution is a superposition of decreasing exponentials, the solution of the non-Markovian master equation may involve oscillations.[33] The damped oscillations coming from the destruction term have been observed in a remarkable experiment by Strombotne and Hahn.[34] These authors studied the nuclear magnetism which appears after a sudden magnetization of an ordered spin system prepared by adiabatic demagnetization. After the sudden application of the external field H_0, the Hamiltonian is

$$\mathscr{H} \simeq \mathscr{H}_Z + \sum_{s=0,\pm1,\pm2} V^{(s)}$$

The density matrix at the initial time is represented by

$$\rho \simeq [1 - \sum_{s=0,\pm1,\pm2} V^{(s)}/kT](\mathrm{Tr}1)^{-1} \tag{73}$$

where clearly the diagonal element $V^{(0)}$ and the off-diagonal elements $V^{(s\neq0)}$ are of the same order. The calculations are best performed in the interaction representation (see, for example, Refs. 9 and 25). If we denote by $\tilde{A}(t)$ the interaction representation of A, then the formal solution of the equation of motion is

$$\tilde{\rho}(t) = \exp\left[\frac{-i}{\hbar}\int_0^t \sum_{s\neq0} \tilde{V}^{(s)}(t')dt'\right][1 - \sum_s V^{(s)}/kT](\mathrm{Tr}1)^{-1} \times \exp\left[\frac{i}{\hbar}\int_0^t \sum_s \tilde{V}^{(s)}(t')dt'\right] \tag{74}$$

This is a series in powers of $\hbar\Delta\omega/kT$ and $\Delta\omega/\omega_0 = H_l/H_0$, where H_l is the local field. The first terms leading to a macroscopic magnetization $\bar{M}_z$ come from the off-diagonal elements of ρ at time zero, the $V^{(s\neq 0)}$ terms. They describe the destruction by the interactions of the initial correlations. According to the general theory, this phenomenon takes place in a time of the order of the collision time. When the applied field H_0 is much larger than the local field H_l, the time evolution involves two steps. In the first one, a macroscopic magnetization $\bar{M}_z$ is built up in an oscillatory way from the initial correlations described by the $V^{(s\neq 0)}$ terms, i.e. at the expense of the dipole–dipole energy.[9] This can be seen from the values of the diagonal elements of ρ. Working in the representation defined by Eq. (21) the first terms of the expansion of Eq. (74) give the following expression, valid for times of the order of $(\Delta\omega)^{-1}$:

$$\begin{aligned}\mathrm{Tr1}\langle \mathrm{M}, n|\rho|M, n\rangle &= 1 - E_{M,n}/kT \\ &- \frac{4}{kT}\sum_{s=\pm 1,\pm 2}\sum_{n'}\langle M, n|V^{(s)}|M+s, n'\rangle\langle M+s, n'|V^{(-s)}|M, n\rangle \\ &\times (s\hbar\omega_0)^{-1}\sin^2\left(\frac{s\omega_0}{2} + \frac{\Delta^s_{nn'}}{2\hbar}\right)t + O\left[\frac{\hbar\Delta\omega}{kT}\left(\frac{\Delta\omega}{\omega_0}\right)^2\right] \qquad (75)\end{aligned}$$

where $\Delta^s_{nn'} = E_{M+s,n} - E_{M,n'}$. The system has an oscillating magnetic moment $\bar{M}_z$. These oscillations are damped in a time of the order of $(\Delta\omega)^{-1}$ and $\bar{M}_z$ reaches an intermediate value. In the second and much longer step of the evolution, $\bar{M}_z$ varies more slowly and reaches its final equilibrium value. The initial, intermediate, and final states are respectively characterized by the following density matrices:

$$(\mathrm{Tr1})^{-1}\left(1 - \sum_{s=0,\pm 1,\pm}\frac{V^{(s)}}{kT_i}\right), \quad (\mathrm{Tr1})^{-1}\left(1 - \frac{\mathscr{H}_\mathrm{Z}}{kT_\mathrm{Z}} - \frac{V^{(0)}}{kT_i}\right)$$

and

$$(\mathrm{Tr1})^{-1}\exp\left[-\frac{\mathscr{H}_\mathrm{Z} - V^{(0)}}{kT_f}\right]$$

where T_i is the initial temperature, T_Z a time-dependent Zeeman temperature, and T_f the final equilibrium temperature. These two steps have been observed by Strombotne,[35] but he does not explicitly use the two temperatures in his discussions. The terms

of ρ we have just considered, leading to an oscillating macroscopic magnetization, are of the order of $(\hbar\Delta\omega/kT) \cdot (\Delta\omega/\omega_0)$. On the other hand, the terms which we have not written down and which are called the collision terms in the general formalism because they express how the diagonal elements of ρ depend on the other diagonal elements are of order $(\hbar\Delta\omega/kT)(\Delta\omega/\omega_0)^2$. These terms are responsible for the equalization of the Zeeman and the dipole–dipole temperatures. They are not observable in Strombotne's experiments because the system has been prepared by a complete adiabatic demagnetization and has therefore no macroscopic magnetization. It would be interesting to observe them starting from a state obtained by sudden demagnetization and having an initial magnetic moment. Then the collision term would also be of the order of $(\hbar\Delta\omega/kT) \cdot (\Delta\omega/\omega_0)$.

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ON THE COMPARISON BETWEEN TWO GENERALIZED BOLTZMANN EQUATIONS

J. BROCAS*

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* Aspirant at the Fonds National de la Recherche Scientifique of Belgium.

I. INTRODUCTION

Twenty years ago, Bogolubov[3] developed a method of generalizing the Boltzmann equation for moderately dense gases. His idea was that if one starts with a gas in a given initial state, its evolution is at first determined by the initial conditions. After a lapse of time—of the order of several collision times—the system reaches a state of quasi-equilibrium which does not depend on the initial conditions and in which the n-particle distribution functions ($n \geqslant 2$) depend on the time only through the one-particle distribution function. With these simple statements Bogolubov derived a Boltzmann equation taking into account delocalization effects due to the finite radius of the particles, and he also established the formal relations that the n-particle distribution function has to obey.

Twelve years later, Choh and Uhlenbeck[6] published the first explicit generalization of the Boltzmann equation involving triple collisions. Their work rests on Bogolubov's ideas and formal results. Green[11] and Rice, Kirkwood, and Harris[26] also obtained the triple collision equation by other methods.

The most recent effort in this direction is the work of Cohen,[8] who established a systematic generalization of the Boltzmann equation. This author obtained the explicit forms of the two-, three-, and four-particle collision terms. His approach is formally very similar to the cluster expansion of Mayer in the equilibrium case.

At the same time, Prigogine and his co-workers[14,15,17] developed a general theory of non-equilibrium statistical mechanics. They derived a non-Markovian evolution equation for the velocity distribution function. Their results contain a generalization of the Boltzmann equation for arbitrary concentration and coupling parameter. This generalization is the long-time limit of their evolution equation.

It was therefore useful and interesting to compare explicitly the derivations of Bogolubov, Choh–Uhlenbeck, and Cohen (which we shall call the streaming operators method) and the results of Prigogine's theory. Part of this comparison has been made previously.

(a) In the case of a dilute gas, it has been proved that the two-body collision operator obtained by Prigogine and his co-workers

is equivalent to the collision term of the Boltzmann equation.[16] On the other hand, it can be shown[7] that the two-body term as derived by Bogolubov, Choh and Uhlenbeck, and Cohen is identical with Boltzmann's collision term.

(b) For the first density correction, Résibois[21,23] established the equivalence between Cohen's three-body result and the corresponding approximation for the long-time evolution equation derived by Prigogine and his co-workers.

(c) Stecki[28] has developed a perturbation expansion of Bogolubov's results and Stecki and Taylor[29] have proved that it is equivalent to the same expansion for the long-time evolution equation in Prigogine's version.

However, some problems remain unsolved. The three- and four-body results of Choh and Uhlenbeck and of Cohen, respectively, have to be compared with the corresponding expressions in the Prigogine's theory. Furthermore, for any concentration, one has to see how the systematic generalization of the Boltzmann equation derived by Cohen is related to the long-time evolution equation in Prigogine's theory. The aim of this work is to throw some light on these points.

In Section II, we summarize the ideas and the results of Bogolubov,[3] Choh and Uhlenbeck,[6] and Cohen.[8] Bogolubov and Choh and Uhlenbeck solved the hierarchy equations and derived two- and three-body generalized Boltzmann operators; Cohen used a cluster expansion method and obtained two-, three-, and four-body explicit results which he was able to extend to arbitrary concentrations.

Section III is devoted to Prigogine's theory.[14] We write down the general non-Markovian master equation. This expression is non-instantaneous because it takes account of the variation of the velocity distribution function during one collision process. Such a description does not exist in the theories of Bogolubov,[3] Choh and Uhlenbeck,[6] and Cohen.[8] We then present two special forms of this general master equation. On the one hand, when one is far from the initial instant the variation of the distribution functions becomes slower and slower and, in the long-time limit, the non-Markovian master equation reduces to the Markovian generalized Boltzmann equation. On the other hand, the transport coefficients are always calculated in situations which are

stationary (e.g., electrical conductivity) or quasi-stationary (e.g., thermal conductivity in a system where the inhomogeneities disappear on a hydrodynamic time scale). In both examples, we only need the transport operator because the distribution functions do not vary.

In Section IV, we develop the former results and we study the structure of the transport operator and of the generalized Boltzmann operator. We also analyse the irreducibility condition which appears in Prigogine's theory by using the graphs of equilibrium statistical mechanics.

Finally, in Section V, we compare the results of Bogolubov,[3] Choh and Uhlenbeck,[6] and Cohen[8] with the generalized Boltzmann equation in Prigogine's formalism. The equivalence of the two methods is well known for the two-body and Cohen's three-body results;[23] the demonstration of the same indentity is extended to the three-body results of Choh and Uhlenbeck and to Cohen's four-body expression. We also present the principles of the extension of this comparison for arbitrary concentration.

In addition, we have calculated the three-body transport operator using Cohen's formalism and, of course, we find an expression which is different from the generalized Boltzmann operator in the same formalism.

Finally, we note an important difference between the two equivalent versions of the generalized Boltzmann equation: the n-body contributions in the results of Choh and Uhlenbeck[6] and of Cohen[8] contain for $n \geqslant 3$ several terms which separately diverge but which compensate each other. Such artificial divergences do not exist in Prigogine's compact expressions because of a dynamical irreducibility condition which eliminates the configurations where the particles, having interacted, are infinitely separated and then interact again (see also note on p. 381).

Apart from the main text, four appendices have been presented. Two of them are devoted to detailed calculations (A.I and A.II). The others (A.III and A.IV) give the major ideas of two derivations which are closely related to our subject but proceed in a rather different way: A.III reports the results of Stecki and Taylor, [28,29] and A.IV contains a very compact proof of the equivalence between the results of Cohen and of Prigogine; this proof has been obtained very recently by P. Resibois and the

author,[4a] it is valid for any concentration but is certainly less explicit than that presented here.

II. THE STREAMING OPERATORS METHODS

In this section, we present the principal results obtained by Bogolubov,[3] Choh and Uhlenbeck,[6] and Cohen.[8]

The Bogolubov[3] method reduces the equations of the hierarchy by making the fundamental hypothesis that the system, starting from the given initial conditions, rapidly attains a "kinetic" regime of quasi-equilibrium in which the distribution functions for more than one particle no longer depend upon the time except through the distribution function of one particle. This time-dependence is made explicit by imposing a boundary condition which states that the correlations are of finite range at the initial instant. Bogolubov derives some formal expressions for the distribution function of s particles. He also demonstrates the Boltzmann equation and his result takes into account the variations of the one-particle distribution function over molecular distances.

Choh and Uhlenbeck[6] developed Bogolubov's ideas and extended his formal results. They established a generalized Boltzmann equation which takes account of three-particle collisions. The extension of their results to higher orders in the concentration poses no problem in principle, but it appears difficult, in this formalism, to write *a priori* the collision term with an arbitrary number of particles.

One such systematic generalization was obtained by Cohen,[8] whose method is now given: the point of departure was the expansion in "clusters" of the non-equilibrium distribution functions. This procedure is formally analogous to the series expansion in the activity where the integrals of the Ursell cluster functions at equilibrium appear in the coefficients. Cohen then obtained two expressions in which the distribution functions of one and two particles are given in terms of the solution of the Liouville equation for one particle. The elimination of this quantity between these two expressions is a problem which presents a very full formal analogy with the elimination (at equilibrium) of the activity between the Mayer equation for the concentration and the series

expansion in powers of the activity of the equilibrium distribution functions. This virial expansion of the non-equilibrium distribution functions allowed Cohen to write down the evolution equation for the one-particle distribution function. We shall recall these results, which include the collisions of two, three, and four particles, and state the rules formulated by Cohen for generalizing these expressions to all orders in the concentration.

A. Bogolubov's Method

Let us consider a gas of N particles of mass m enclosed in a container of volume V. The Hamiltonian of the system is:

$$H = \sum_{j=1}^{N} \frac{p_j^2}{2m} + \lambda \sum_{i>j=1}^{N} V_{ij} \tag{1}$$

The first term is the total kinetic energy of the particles, whose individual momenta are $\mathbf{p}_j = m\mathbf{v}_j$. The second term is the potential energy; $V_{ij} = V_{ij}(|\mathbf{r}_i - \mathbf{r}_j|)$ is the interaction energy of particle i with particle j when their respective positions are $\mathbf{r}_i$ and $\mathbf{r}_j$. The parameter λ measures the intensity of this coupling.

The distribution function $\rho_N(\mathbf{x}_1 \ldots \mathbf{x}_N, t)$ in the $6N$-dimensional phase space represents the probability of finding particle i with phase $\mathbf{x}_i = \mathbf{r}_i, \mathbf{p}_i$, particle j with phase $\mathbf{x}_j = \mathbf{r}_j, \mathbf{p}_j$, etc., . . . at the instant t. This function obeys the Liouville equation

$$i \frac{\partial \rho_N(t)}{\partial t} = L_N \rho_N(t) = (L_N^0 + \lambda \delta L_N)\rho_N(t) \tag{2}$$

and is normalized to unity:

$$\int d\mathbf{x}_1 \ldots \int d\mathbf{x}_N \rho_N(t) = 1 \tag{3}$$

In Eq. (2), L_N is the Liouville operator, which is decomposed into two terms:

$$L_N^0 = -i \sum_{j=1}^{N} \mathbf{v}_j \cdot \frac{\partial}{\partial \mathbf{r}_j} \tag{4}$$

is associated with the kinetic energy, while

$$\delta L_N = i \sum_{i>j=1}^{N} \frac{\partial V_{ij}}{\partial \mathbf{r}_i} \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j} \right) = \sum_{i>j=1}^{N} \delta L^{(ij)} \tag{5}$$

is due to the interactions.

The Liouville equation can be integrated over all the phases $\mathbf{x}_j = \mathbf{r}_j, \mathbf{p}_j$ except those of the sub-group of particles $1, 2, \ldots, s$. One obtains then:

$$i\frac{\partial f_s}{\partial t} = L_s f_s + \lambda \int d\mathbf{x}_{s+1} \sum_{i=1}^{s} \delta L^{(i,s+1)} f_{s+1}(\mathbf{x}_1 \ldots \mathbf{x}_{s+1}) \qquad (6)$$

where f_s is the reduced distribution function:

$$f_s(\mathbf{x}_1 \ldots \mathbf{x}_s, t) = \frac{N!}{(N-s)!} \int d\mathbf{x}_{s+1} \ldots \int d\mathbf{x}_N \rho_N(t) \qquad (7)$$

The equation (6) for $s = 1$ connects f_1 to f_2, which is itself connected to f_3. The ensemble of equations (6) constitutes the hierarchy derived independently by Bogolubov, Born, Green, Kirkwood, and Yvon. This hierarchy is equivalent to the Liouville equation and to try to solve it is equivalent to studying the trajectories of 10^{23} particles whose phases at the initial instant are known.

Bogolubov[3] developed a theory which allows the hierarchy to be "cut" and the evolution of f_1 in terms of f_1 itself to be expressed. To do this, he assumed that there are three stages in the evolution with time of a macroscopic gaseous system:

(1) The initial stage, during which the evolution of the system is described by the complete hierarchy and depends upon the initial conditions, has a lifetime of the order of the collision time τ_c.

(2) During the course of the kinetic stage the system forgets its initial conditions and attains a quasi-equilibrium regime independent of its previous history. This is reached after a time τ_r from the initial instant, τ_r being the time in which two successive collisions of the same particle (relaxation time) occur. Bogolubov made the fundamental hypothesis that, in this region, the distribution function for more than one particle depends on the time through the intermediary of f_1:

$$\text{for } s > 1: \qquad f_s(\mathbf{x}_1 \ldots \mathbf{x}_s, t) = f_s(\mathbf{x}_1 \ldots \mathbf{x}_s | f_1(\mathbf{x}_i, t)) \qquad (8)$$

(3) In the final, hydrodynamic stage, the system is described by the density, the average velocity, and the local temperature and evolves towards equilibrium by means of the effect of transport phenomena (conductivity, diffusion, viscosity, . . .). This takes place in times of the order of the hydrodynamic time τ_h,

i.e., the time a "thermal" particle needs to travel the length of the macroscopic gradients.

If we know the form of the functional dependence (8) for $s = 2$, it is clear that the first equation of the hierarchy gives a closed equation for f_1. Bogolubov expressed this dependence by imposing a boundary condition which the solution f_s of the hierarchy must satisfy: for instance, in the homogeneous case to which we will limit the following discussion

$$S^{(s)}_{-\infty}(\mathbf{x}_1 \ldots \mathbf{x}_s) f_s(\mathbf{x}_1 \ldots \mathbf{x}_s | f_1(\mathbf{x}_i, t)) = S^{(s)}_{-\infty}(\mathbf{x}_1 \ldots \mathbf{x}_s) \prod_{j=1}^{s} f_1(\mathbf{x}_j, t) \tag{9}$$

We have used the streaming operators

$$S^{(s)}_t(\mathbf{x}_1 \ldots \mathbf{x}_s) = S^{(1 \cdots s)}_t = \exp[itL_s] \tag{10}$$

whose effect is to transform the phases $(\mathbf{x}^0_1 \ldots \mathbf{x}^0_s)$ of the s particles at the instant $t = 0$ to the phases $(\mathbf{x}_1 \ldots \mathbf{x}_s)$ at the instant t when the s particles are displaced under the influence of their mutual interactions.

The condition (9) expresses the fact that the s particles, whose phases are $\mathbf{x}_1, \ldots, \mathbf{x}_s$ at the instant t, were, in the far distant past $(t = -\infty)$, infinitely separated from each other. There existed at this moment no correlation among these particles and, in these conditions, f_s can be factorized into a product of f_1.

With the aid of the "boundary" condition (9) and by expanding in a series of the concentration $c = N/V$, Bogolubov derived the formal expressions for the distribution function f_s. Moreover, he demonstrated the Boltzmann equation for the homogeneous case and, in the inhomogeneous case, he obtained a Boltzmann equation in which the variation of f_1 over a distance of the order of the range of the forces a is taken into account. This equation agrees with the one proposed by Enskog[10] (see, for example, ref. 5). Choh and Uhlenbeck[6] developed Bogolubov's ideas and extended his formal results. These authors established a generalized Boltzmann equation for the case of a moderately dense gas in which the triple collisions appear explicitly. The contribution of these collisions is, in the homogeneous case,

$$\left(\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(3)} = \lim_{\tau \to \infty} c^2 \int d\mathbf{x}_2 \int d\mathbf{x}_3 A^{(123)}_{-\tau} \prod_{i=1}^{3} \varphi_1(\mathbf{p}_i, t) \tag{11}$$

where we define:

$$A_{-\tau}^{(123)} = \theta_{12} \int_0^\infty dt' S_{-t'}^{(12)} [(\theta_{13} + \theta_{23}) S_{-\tau}^{(123)} - S_{-\tau}^{(12)} (\theta_{13} S_{-\tau}^{(13)} + \theta_{23} S_{-\tau}^{(23)})] \tag{12}$$

and

$$\theta_{ij} = -i\lambda\delta L^{(ij)} \tag{13}$$

We have also introduced the distribution function of the velocities:

$$\varphi_s(\mathbf{p}_1 \ldots \mathbf{p}_s, t) = \frac{(N-s)!}{N!} \int d\mathbf{r}_1 \ldots \int d\mathbf{r}_s f_s(\mathbf{x}_1 \ldots \mathbf{x}_s, t) \tag{14}$$

The method of Bogolubov and of Choh and Uhlenbeck can be extended to higher concentrations. One could, in principle without difficulty, calculate the contributions from collisions with four,* five, . . . etc., particles. It seems difficult, however, in this formalism to write *a priori* the collision term for n particles. Nevertheless, one such systematic generalization appears in a natural fashion in the work of Cohen,[8] which we shall now summarize.

B. Cohen's Method

The point of departure of this method is the "cluster" expansion of the non-equilibrium distribution functions:

$$\frac{1}{c} f_1(\mathbf{x}_1, t) = U_1(\mathbf{x}_1, t) + c \int d\mathbf{x}_2 U_2(\mathbf{x}_1, \mathbf{x}_2, t) + \frac{c^2}{2} \int d\mathbf{x}_2 \int d\mathbf{x}_3 U_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, t) + \ldots \tag{15}$$

$$\frac{1}{c^2} [f_2(\mathbf{x}_1, \mathbf{x}_2, t) - f_1(\mathbf{x}_1, t) f_1(\mathbf{x}_2, t)] = U_2(\mathbf{x}_1, \mathbf{x}_2, t) + c \int d\mathbf{x}_3 U_3(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, t) + \frac{c^2}{2} \int d\mathbf{x}_3 \int d\mathbf{x}_4 U_4(\mathbf{x}_1, \mathbf{x}_2, \mathbf{x}_3, \mathbf{x}_4, t) + \ldots \tag{16}$$

* The contribution from quadruple collisions such as appeared in the Choh–Uhlenbeck version can be found in ref. 8.

These expressions are analogous to the series expansions of the equilibrium distribution functions in terms of the activity in which appear, in the coefficients, the integrals of the Ursell cluster functions U_s (see, for example, ref. 30).

Cohen then introduces four hypotheses which in his theory play essentially the same role as the boundary condition (9) in the Bogolubov method:

(1) The reduced distribution functions at the instant $t = 0$, f_s, are factorized when the s particles are distributed among several groups separated from each other by a distance greater than the range of the forces.

(2) One is interested in the distribution functions for times larger than τ_c (kinetic stage of the Bogolubov method).

(3) The forces are repulsive.

(4) The distribution functions are understood in a "coarse-grained" sense (an average over a small but finite element of volume in momenta space).

Because of these hypotheses, in the homogeneous case, expressions (15) and (16) take the form:

$$\varphi_1(\mathbf{p}_1, t) = \rho_1(\mathbf{p}_1, t) + c\int d\mathbf{x}_2[S_{-t}^{(12)} - 1]\rho_1(\mathbf{p}_1, t)\rho_1(\mathbf{p}_2, t) + \frac{c^2}{2}\int d\mathbf{x}_2\int d\mathbf{x}_3[S_{-t}^{(123)} - \sum_{i>j=1}^{3} S_{-t}^{(ij)} + 2]\rho_1(\mathbf{p}_1, t)\rho_1(\mathbf{p}_2, t)\rho_1(\mathbf{p}_3, t) + \ldots \tag{17}$$

$$\frac{1}{c^2}[f_2(\mathbf{x}_1, \mathbf{x}_2, t) - c^2\varphi_1(\mathbf{p}_1, t)\varphi_1(\mathbf{p}_2, t)] = [S_{-t}^{(12)} - 1]\rho_1(\mathbf{p}_1, t)\rho_1(\mathbf{p}_2, t) + c\int d\mathbf{x}_3[S_{-t}^{(123)} - \sum_{i>j=1}^{3} S_{-t}^{(ij)} + 2]\rho_1(\mathbf{p}_1, t)\rho_1(\mathbf{p}_2, t)\rho_1(\mathbf{p}_3, t) + \ldots \tag{18}$$

where $\rho_1(t)$ is the solution of the Liouville equation for one particle (Eq. 2) with the normalization

$$\int d\mathbf{x}_1\rho_1(\mathbf{x}_1, t) = \frac{1}{V^{N-1}} \tag{19}$$

The next stage is the elimination of the functions $\rho_1(\mathbf{p}_1, t)$ from Eqs. (17) and (18). This problem is formally analogous to that of the elimination, at equilibrium, of the activity from the two equations expressing, respectively, the concentration and

the two-particle distribution function as series in the activity. This virial development of the equilibrium distribution functions has been accomplished in complete generality by Uhlenbeck and Ford[30] and extended to the non-equilibrium case by Cohen,[8] who obtained the following equation of evolution:

$$\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t} = \left(\frac{\partial \varphi_1}{\partial t}\right)^{(2)} + \left(\frac{\partial \varphi_1}{\partial t}\right)^{(3)} + \left(\frac{\partial \varphi_1}{\partial t}\right)^{(4)} + \cdots \tag{20}$$

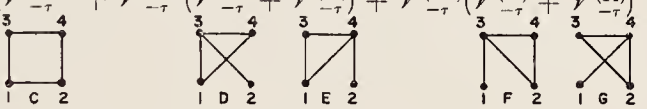
with

$$\left(\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(2)} = c \lim_{\tau \to \infty} \int d\mathbf{x}_2 \theta_{12}[\mathscr{Y}^{(12)}_{-\tau} + 1] \prod_{i=1}^{2} \varphi_1(\mathbf{p}_i, t) \tag{21}$$

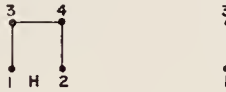
$$\left(\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(3)} = c^2 \lim_{\tau \to \infty} \int d\mathbf{x}_2 \int d\mathbf{x}_3 \theta_{12}[\mathscr{Y}^{(123)}_{-\tau} + \mathscr{Y}^{(13)}_{-\tau}\mathscr{Y}^{(23)}_{-\tau}] \prod_{i=1}^{3} \varphi_1(\mathbf{p}_i, t) \tag{21'}$$

$$\left(\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(4)} = \frac{c^3}{2!} \lim_{\tau \to \infty} \int d\mathbf{x}_2 \int d\mathbf{x}_3 \int d\mathbf{x}_4$$

$$\times \theta_{12}[\mathscr{Y}^{(1234)}_{-\tau} + \mathscr{Y}^{(134)}_{-\tau}(\mathscr{Y}^{(23)}_{-\tau} + \mathscr{Y}^{(24)}_{-\tau}) + \mathscr{Y}^{(234)}_{-\tau}(\mathscr{Y}^{(13)}_{-\tau} + \mathscr{Y}^{(14)}_{-\tau}) \tag{21''}$$



$$+ \mathscr{Y}^{(13)}_{-\tau}\mathscr{Y}^{(24)}_{-\tau}\mathscr{Y}^{(34)}_{-\tau} + \mathscr{Y}^{(14)}_{-\tau}\mathscr{Y}^{(23)}_{-\tau}\mathscr{Y}^{(34)}_{-\tau}] \prod_{i=1}^{4} \varphi_1(\mathbf{p}_i, t)$$



The operators $\mathscr{Y}^{(1\cdots s)}_{-\tau}$ can be obtained from the expressions

$$\mathscr{U}^{(12)}_{-\tau} = \mathscr{Y}^{(12)}_{-\tau} \tag{22}$$

$$\mathscr{U}^{(123)}_{-\tau} = \mathscr{Y}^{(123)}_{-\tau} + \mathscr{Y}^{(12)}_{-\tau}\mathscr{Y}^{(13)}_{-\tau} + \mathscr{Y}^{(12)}_{-\tau}\mathscr{Y}^{(23)}_{-\tau} + \mathscr{Y}^{(13)}_{-\tau}\mathscr{Y}^{(23)}_{-\tau} \tag{22'}$$

$$\mathscr{U}^{(1234)}_{-\tau} = \mathscr{Y}^{(1234)}_{-\tau} + \sum_{(12)} \mathscr{Y}^{(123)}_{-\tau}\mathscr{Y}^{(34)}_{-\tau} + \sum_{(12)} \mathscr{Y}^{(12)}_{-\tau}\mathscr{Y}^{(23)}_{-\tau}\mathscr{Y}^{(34)}_{-\tau} + \sum_{(4)} \mathscr{Y}^{(12)}_{-\tau}\mathscr{Y}^{(13)}_{-\tau}\mathscr{Y}^{(14)}_{-\tau} \tag{22''}$$

which are the analogues for non-equilibrium of the Husimi developments of the cluster functions U_l (see ref. 30). For each product of $\mathscr{Y}$ it is necessary to sum over the many different arrangements of the indices of the particles (two arrangements

are identical if, by permutation of the indices, the connections between the $\mathscr{V}$ are not changed). For each term, the number in parentheses beneath the summation sign indicates the number of different arrangements.

The operators $\mathscr{U}_{-\tau}^{(1\,\cdots\,s)}$ are defined starting from the streaming operators in the same way as are the equilibrium Ursell functions starting from the functions ρ_s (with $\rho_1 \equiv 1$):

$$\mathscr{U}_{-\tau}^{(1)} \equiv 1 \tag{23}$$

$$\mathscr{U}_{-\tau}^{(12)} = S_{-\tau}^{(12)} - 1 \tag{23'}$$

$$\mathscr{U}_{-\tau}^{(123)} = S_{-\tau}^{(123)} - S_{-\tau}^{(12)} - S_{-\tau}^{(13)} - S_{-\tau}^{(23)} + 2 \tag{23''}$$

$$\mathscr{U}_{-\tau}^{(1234)} = S_{-\tau}^{(1234)} - \Sigma S_{-\tau}^{(123)} - \Sigma S_{-\tau}^{(12)} S_{-\tau}^{(34)} + 2\Sigma S_{-\tau}^{(12)} - 6 \tag{23'''}$$

where the Σ are over the permutations of the particles.

If each Husimi operator $\mathscr{V}_{-\tau}^{(1\,\cdots\,s)}$ is represented by a polygon of s sides, the generalization of Eqs. (21) can be formulated in the following manner: $(\partial\varphi_1/\partial t)^{(n)}$ will be given by the sum of the 1,2-irreducible graphs with n points. Each graph will then be a chain comprising n_2 lines, n_3 triangles, n_4 squares, etc., ... These polygons, taken two by two, have only a single vertex in common. If with each vertex one associates the index of one of the n particles of the process studied, the particles 1 and 2 will belong, severally, to the polygons which lie at the two extremities of the chain. Apart from the polygons themselves, the graphs do not comprise any closed chain. Moreover, there are no articulation points (points such that, if one makes a cut on them one separates the diagram into two parts: the chain which connects points 1 and 2 and an "appendage"). The graphs given under each of the terms of the expressions (21) illustrate this.

Equations (20) and (21) and the rule that we have just stated then constitute the systematic generalization of the Boltzmann equation in the formalism of Cohen. We can, with the aid of Eqs. (22), calculate the $\mathscr{V}_{-\tau}^{(1\,\cdots\,s)}$ in terms of $\mathscr{U}_{-\tau}^{(1\,\cdots\,s')}$. These are then expressed by means of the $S_{-\tau}^{(1\,\cdots\,s'')}$. The result, substituted in the relations (21), will give:

$$\left(\frac{\partial\varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(n)} = c^{n-1} \lim_{\tau\to\infty} \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_n B_{-\tau}^{(1\,\cdots\,n)} \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i, t) \tag{24}$$

$$B^{(12)}_{-\tau} = \theta_{12} S^{(12)}_{-\tau} \tag{25}$$

$$B^{(123)}_{-\tau} = \theta_{12}[S^{(123)}_{-\tau} - S^{(12)}_{-\tau}(S^{(13)}_{-\tau} + S^{(23)}_{-\tau} - 1)] \tag{25'}$$

$$\begin{aligned} B^{(1234)}_{-\tau} = \frac{1}{2!}\theta_{12}[&S^{(1234)}_{-\tau} - S^{(123)}_{-\tau}(S^{(14)}_{-\tau} + S^{(24)}_{-\tau} + S^{(34)}_{-\tau} - 2) \\ &- S^{(124)}_{-\tau}(S^{(13)}_{-\tau} + S^{(23)}_{-\tau} + S^{(34)}_{-\tau} - 2) - S^{(12)}_{-\tau}(S^{(134)}_{-\tau} + S^{(234)}_{-\tau} \\ &- 2S^{(13)}_{-\tau}S^{(14)}_{-\tau} - 2S^{(23)}_{-\tau}S^{(24)}_{-\tau} - S^{(13)}_{-\tau}S^{(34)}_{-\tau} - S^{(23)}_{-\tau}S^{(34)}_{-\tau} \\ &- S^{(13)}_{-\tau}S^{(24)}_{-\tau} - S^{(14)}_{-\tau}S^{(23)}_{-\tau} - S^{(14)}_{-\tau}S^{(34)}_{-\tau} - S^{(24)}_{-\tau}S^{(34)}_{-\tau} \\ &+ 2S^{(14)}_{-\tau} + 2S^{(24)}_{-\tau} + 2S^{(13)}_{-\tau} + 2S^{(23)}_{-\tau} + S^{(34)}_{-\tau} - 2)] \end{aligned} \tag{25''}$$

The explicit expressions (25) will be compared with the results of Prigogine and his collaborators, whose approach we shall now present.

III. THE PRIGOGINE THEORY

The main lines of the Prigogine theory[14,15,17] are presented in this section. A perturbation calculation is employed to study the N-body problem. We are interested in the asymptotic solution of the Liouville equation in the limit of a large system. The resolvent method is used (the resolvent is the Laplace transform of the evolution operator of the N particles). We recall the equation of evolution for the distribution function of the velocities. It contains, first, a part which describes the destruction of the initial correlations; this process is achieved after a finite time if the correlations have a finite range. The other part is a collision term which expresses the variation of the distribution function at time t in terms of the value of this function at time t', where $t \geqslant t' \geqslant t - \tau_c$. This expresses the fact that the system has a memory because of the finite duration of the collisions which renders the equations non-instantaneous.

We then write down the equation of evolution for the distribution function in the limit of long times. This is the generalized Boltzmann equation, which, this time, is instantaneous because, in the limit of long times, the variation of the distribution function during the time interval τ_c becomes slow. Also, in the long-time limit, we briefly discuss the equation which gives the correlations.

The essential characteristic of the equilibrium correlations is that they originate in a system starting from non-correlated states. We recall also that the correct form of the equilibrium correlations can be obtained if one admits that for long times the velocity distribution function takes a Maxwellian form.

Finally, we attack the problem of the transport coefficients, which, by definition, are calculated in the stationary or quasi-stationary state. The variation of the distribution functions during the time τ_c is consequently rigorously nil, which allows us to calculate these coefficients from more simple quantities than the generalized Boltzmann operators which we call asymptotic cross-sections or transport operators.

A. Generalities

The method developed by I. Prigogine and his collaborators (see, for example, ref. 14) is a perturbation calculation to study the N-body problem. The point of departure is the Liouville equation (2) of which one looks for the solution in the limit of a large system:

$$N \to \infty; \qquad V \to \infty; \qquad c = \frac{N}{V} \text{ finite} \tag{26}$$

Let us introduce the resolvent operator, a function of the complex variable z:

$$R_N(z) = (L_N - z)^{-1} \tag{27}$$

which satisfies the identity:

$$R_N(z) = (L_N^0 - z)^{-1} - (L_N^0 - z)^{-1}\lambda\delta L_N(L_N - z)^{-1} \tag{28}$$

By iteration of this "operator integral equation" one obtains the following series expansion in the coupling parameter λ:

$$R_N(z) = (L_N^0 - z)^{-1} \sum_{n=0}^{\infty} [-\lambda\delta L_N(L_N^0 - z)^{-1}]^n \tag{29}$$

On the other hand, the solution of the Liouville equation (2) is written formally:

$$\rho_N(t) = \exp(-iL_N t)\rho_N(0) \tag{30}$$

so, in terms of $R_N(z)$ which is the Laplace transform of $\exp(-iL_N t)$,

$$\rho_N(t) = -\frac{1}{2\pi i}\int_C dz \frac{\exp(-izt)}{L_N - z}\rho_N(0) \tag{31}$$

where the contour C in the complex plane is shown in Fig. 1 and is situated above all the singularities of $(L_N - z)^{-1}$.

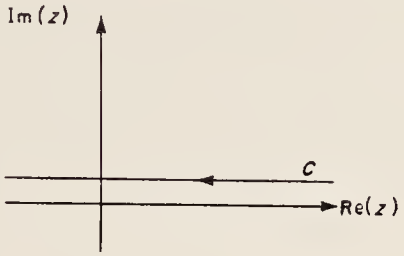


Fig. 1. The contour C.

Let us also introduce the eigenfunctions of the unperturbed Liouville operator (4)

$$\begin{aligned}\varphi_{\{\mathbf{k}\}}(\{\mathbf{r}\}) &= V^{-N/2}\exp\left[i\sum_{j=1}^{N}\mathbf{k}_j\cdot\mathbf{r}_j\right] \\ &= \langle\{\mathbf{r}\}|\{\mathbf{k}\}\rangle\end{aligned} \tag{32}$$

in the Dirac[9] notation ($\varphi_{\{\mathbf{k}\}}(\{\mathbf{r}\})$ being configuration representation of the eigenvector $|\{\mathbf{k}\}\rangle$). Let us define the Fourier coefficient:

$$\rho_{\{\mathbf{k}\}}(\mathbf{p}_1 \cdots \mathbf{p}_N, t) = V^{-N/2}\int d\mathbf{r}_1 \cdots \int d\mathbf{r}_N \rho_N(t)\exp\left[-i\sum_{j=1}^{N}\mathbf{k}_j\cdot\mathbf{r}_j\right] \tag{33}$$

which is the projection of $\rho_N(t)$ on the eigenvector $|\{\mathbf{k}\}\rangle$. These coefficients satisfy the relations:

$$\rho_{\{\mathbf{k}\}}(\mathbf{p}_1 \cdots \mathbf{p}_N, t) = -\frac{1}{2i\pi}\int_C dz \exp(-izt)\sum_{n=0}^{\infty}\sum_{\{\mathbf{k}'\}}\langle\{\mathbf{k}\}|(L_N^0 - z)^{-1}$$

$$\{-\lambda\delta L_N(L_N^0 - z)^{-1}\}^n|\{\mathbf{k}'\}\rangle\rho_{\{\mathbf{k}'\}}(\mathbf{p}_1 \cdots \mathbf{p}_N, 0) \tag{34}$$

that one obtains by combining relations (29), (31), and (33). This finite system of equations, which connects each Fourier coefficient at the instant t to all the coefficients at the initial instant, is strictly equivalent to the Liouville equation (2).

However, if one studies the velocity distribution $\rho_{\{0\}}(\mathbf{p}_1 \ldots \mathbf{p}_N, t)$ one can introduce the following operators whose physical sense will become clear in the following (see refs. 14 and 24):

$$\Psi'_{00}(z) = \sum_{n=2}^{\infty} (-\lambda)^n \langle 0 | \delta L_N ((L_N^0 - z)^{-1} \delta L_N)^{n-1} | 0 \rangle' \tag{35}$$

which is the sum of all the terms of Eq. (34) which allow a "transition" from an initial vacuum state (where all the wave vectors $\mathbf{k}$ are zero) to a final vacuum state. The "prime" in Eq. (35) and in the following expressions signifies that this transition is effected without passing through the vacuum. We can also write

$$C_{\{\mathbf{k}\}0}(z) = \sum_{n=1}^{\infty} (-\lambda)^n \langle \{\mathbf{k}\} | [(L_N^0 - z)^{-1} \delta L_N]^n | 0 \rangle' \tag{36}$$

and

$$D_{0\{\mathbf{k}\}}(z) = \sum_{n=1}^{\infty} (-\lambda)^n \langle 0 | [\delta L_N (L_N^0 - z)^{-1}]^n | \{\mathbf{k}\} \rangle' \tag{37}$$

which describe, respectively, the creation of a correlation $\{\mathbf{k}\}$ starting initially from the vacuum and the destruction of the initial correlation $\{\mathbf{k}\}$ ending in the vacuum without, in either case, passing through the vacuum.

With the aid of these operators, Eq. (34) can be put into the form:

$$\rho_{\{0\}}(t) = -\frac{1}{2\pi i} \int_C dz \exp(-izt) \sum_{m=0}^{\infty} \left(-\frac{1}{z}\right) \left[\Psi'^{+}_{00}(z) \left(\frac{1}{-z}\right)\right]^m \times \{\rho_{\{0\}}(0) + \sum_{\{\mathbf{k}\} \neq 0} D^{+}_{0\{\mathbf{k}\}}(z) \rho_{\{\mathbf{k}\}}(0)\} \tag{38}$$

where we have omitted writing the arguments $\mathbf{p}_1, \ldots, \mathbf{p}_N$ of the functions $\rho_{\{0\}}(t)$. The functions $\Psi'_{00}(z)$, $C_{\{\mathbf{k}\}0}(z)$, and

$$\sum_{\{\mathbf{k}\} \neq 0} D_{0\{\mathbf{k}\}}(z) \rho_{\{\mathbf{k}\}}(0)$$

are analytic in z over all the complex plane except on the real axis where they possess a finite discontinuity. As far as the destruction operator is concerned, this property is only realized for a certain class of initial conditions: those where the range of correlations in configuration space is finite. The plus signs which

appear above the operators in Eq. (38) indicate that the functions of the complex variable z are defined by Eqs. (35), (36), and (37) only in the upper half-plane and are analytically continued into the lower half-plane. We shall assume that their analytic continuation comprises poles of finite order at $z = z_i$ with the typical property

$$\operatorname{Im} z_i = -1/\tau_c \tag{39}$$

This last property is verified for certain laws of interaction. It is neither general nor necessary to obtain results of the same type as those which we shall present. In the following discussion Eq. (39) will be considered as a sufficient condition for the equations of evolution which we shall write down to be valid.

B. Evolution and Transport Equations—*H*-Theorem

The master equation affects the evolution of the distribution function of all the velocities and is written:

$$\frac{\partial \rho_{\{0\}}(t)}{\partial t} = D^+_{0\{\mathbf{k}\}}(t, \rho_{\{\mathbf{k}\}}(0)) + \int_0^t dt' G^+_{00}(t - t')\rho_{\{0\}}(t') \tag{40}$$

where

$$D^+_{0\{\mathbf{k}\}}(t, \rho_{\{\mathbf{k}\}}(0)) = -\frac{1}{2\pi}\int_C dz \exp(-izt) \sum_{\{\mathbf{k}\}\neq 0} D^+_{0\{\mathbf{k}\}}(z)\rho_{\{\mathbf{k}\}}(0) \tag{41}$$

$$G^+_{00}(t) = -\frac{1}{2\pi i}\int_C dz \exp(-izt)\Psi^+_{00}(z) \tag{42}$$

We also define

$$C^+_{\{\mathbf{k}\}0}(t) = -\frac{1}{2\pi}\int_C dz \exp(-izt)C^+_{\{\mathbf{k}\}0}(z) \tag{43}$$

These operators possess the following properties

$$\text{if } t \to \infty\text{: } G^+_{00}(t), \quad C^+_{\{\mathbf{k}\}0}(t) \quad \text{and} \quad D^+_{0\{\mathbf{k}\}}(t, \rho_{\{\mathbf{k}\}}(0)) \to 0 \tag{44}$$

Hence, we can interpret the equation of evolution (40). The first term expresses the fact that the correlations which exist

at time $t = 0$ are destroyed during the course of a process in which the initially correlated particles interact among themselves. Thus, the initial correlations contribute to the evolution of $\rho_{\{0\}}$ at the instant t. However, for times long removed from $t = 0$ the system forgets its initial correlations: this is expressed by the property (44) of $D^{+}_{0\{\mathbf{k}\}}(t)$ and follows from our hypothesis about the finite range of the initial correlations. Indeed, after a finite time, two initially correlated particles are already sufficiently separated from each other to cease interaction with each other. The destruction of the correlations takes a finite time and they no longer contribute to the evolution of $\rho_{\{0\}}$ at a later instant.

The second term of Eq. (40) gives the contribution from collisions. These are non-instantaneous processes since the variation of $\rho_{\{0\}}$ at the time t depends on the value of this function at the earlier instant t'. The evolution is non-Markovian and the system remembers its earlier history. However, this memory extends only over a finite period, as one can see from the expression (44) for the kernel $G^{+}_{00}(t)$. This results from supposing that the poles z_i are not infinitesimally close to the real axis and thus that the collision time τ_c is finite (see Eq. (39)).

For long times Eq. (40) assumes a Markovian form and will be called the generalized Boltzmann equation:

$$\frac{\partial \rho_{\{0\}}(t)}{\partial t} = i\Omega(i0)\Psi^{+}_{00}(i0)\rho_{\{0\}}(t) \tag{45}$$

Equation (40) was non-Markovian because $\rho_{\{0\}}(t)$ varied appreciably during the collision. When one is far from the initial instant, this variation becomes slower and slower and for sufficiently long times all the effects of the variation of $\rho_{\{0\}}(t)$ during the finite duration of the collisions can be described by the operators $\Omega(i0)$ defined by the relations:

$$\Omega(z) = \sum_{l=0}^{\infty} \Omega_l(z) \tag{46}$$

$$\left.\begin{aligned} &\Omega_0(i0) = 1 \\ &\text{and for } l \neq 0 \\ &\Omega_l(z) = -\frac{1}{l}\sum_{j=0}^{l-1} \frac{\partial}{\partial z}\left[\Omega_{l-j-1}(z)\Psi^{+}_{00}(z)\right]\Omega_j(z) \end{aligned}\right\} \tag{47}$$

Moreover, for long times, the Fourier components with a finite number of non-zero wave vectors are given by the equation:

$$\rho_{\{\mathbf{k}\}}(t \to \infty) = \lim_{t \to \infty} \int_0^t dt' C^+_{\{\mathbf{k}\}0}(t') \rho_{\{0\}}(t - t') \tag{48}$$

which signifies that equilibrium correlations are created in the system starting from non-correlated states, after the initial correlations have been dissipated (see Eq. (44)).

One can show (see, for example, ref. 24) that the Maxwellian distribution of velocities

$$\Phi_0 = \prod_{i=1}^{N} \exp\left(-\frac{p_i^2}{2mkT}\right) \tag{49}$$

where k is Boltzmann's constant and T is the temperature, is an eigenfunction of the operator of the member on the right of Eq. (45) with the eigenvalue zero. In order to demonstrate an "H-theorem", i.e.,

$$\rho_{\{0\}}(t \to \infty) = \Phi_0 \tag{50}$$

it will be necessary to establish that the other eigenfunctions of Eq. (45) correspond to eigenvalues whose real parts are negative. Indeed, if this property were verified, only the null eigenvalue would contribute to $\rho_{\{0\}}(t \to \infty)$ and the "H-theorem" would be demonstrated. Unfortunately, the property in question can only be established to the lowest order in λ or in c and, consequently, one has to assume at present that it remains true as λ or c increase in order to obtain the "H-theorem", i.e., that Φ_0 is the only stationary solution of Eq. (45).

Finally, if Eq. (50) is admitted, one can show that (48) gives the correct form for the equilibrium correlations:[1,12,24] the dynamical approach (48) is then equivalent to the expansion in equilibrium clusters (see, for example, ref. 13).

In addition to the general problem of the kinetics of the approach towards equilibrium, the statistical mechanics of irreversible phenomena concern in particular the study of transport phenomena. The latter are calculated in a stationary or quasi-stationary form (the distribution functions do not vary or vary in hydrodynamic fashion). Therefore, let us consider (see, for

example, ref. 17) the case of a homogeneous system composed of particles of charge e immersed in an electric field **E**. For calculation of the electrical conductivity, a knowledge of $\rho_{\{0\}}(t)$ suffices and in the stationary situation one has:

$$\frac{\partial \tilde{\rho}^{\{0\}}}{\partial t} = \frac{\partial \tilde{\rho}_{\{0\}}}{\partial t}\bigg|_{\text{collisions}} + \frac{\partial \tilde{\rho}_{\{0\}}}{\partial t}\bigg|_{\text{field}} = 0 \tag{51}$$

The stationary condition allows $\rho_{\{0\}}(t)$ to be replaced by $\rho_{\{0\}}(t')$ in the collision term (40) and the upper limit of the integration over time to be extended to infinity, because the instant t when the system is stationary is very far removed from the initial instant. One then obtains:

$$\left[\int_0^\infty d\tau G_{00}^{+}(\tau)\right] \tilde{\rho}_{\{0\}} \simeq \frac{\partial \tilde{\rho}_{\{0\}}}{\partial t}\bigg|_{\text{collisions}} \tag{52}$$

or again, if the field is weak, i.e., if $\rho_{\{0\}} = \Phi_0 + E\Phi_1$,

$$E\Psi_{00}^{+}(i0)\,\Phi_1 \simeq \frac{\partial \tilde{\rho}_{\{0\}}}{\partial t}\bigg|_{\text{collisions}} \tag{53}$$

One sees then, by this simple example, that one can obtain Φ_1 and the electrical conductivity by knowing only $\Psi_{00}^{+}(i0)$. This result has been demonstrated rigorously by Balescu.[2]

The difference between Eqs. (45) and (53) comes from the stationary condition which allows the variation of the distribution function during the collision processes to be neglected and the statement $\Omega(i0) = 1$ to be made.

IV. THE STRUCTURE OF THE TRANSPORT OPERATOR AND OF THE GENERALIZED BOLTZMANN OPERATOR

In this section we shall explain somewhat the results which we have just presented. We are interested this time in the evolution equation for the one-particle distribution function. We write down the virial series expansion of the transport equation and we recall that every contribution to this equation is proportional to V^{-n+d}, where n is the number of particles which are involved

in the collision and if they can be separated into d clusters which do not affect each other. The dynamical processes which appear in the transport operator are called connected if $d = 1$ and non-connected otherwise. In fact, since the transport operator is integrated over all the velocities except one, only the connected processes contribute to the transport equation.

We study next the dynamical irreducibility condition which appeared in the definition of the transport operator. It eliminates from this quantity the reducible collision processes where the particles coming from infinity interact, recede to an infinite distance from one another, and then interact again. We define an extended transport operator from which the irreducibility condition is eliminated and which involves this time the reducible collisions. The relation between the transport operator and the extended transport operator is made explicit by means of a correspondence between the dynamical processes and the Mayer graphs for equilibrium. In this respect, we demonstrate, in these graphs, the importance of the role of the articulation points.

Finally, we study the structure of the generalized Boltzmann operator. It can be expressed in terms of the transport operator, which allows one to obtain the virial expansion of the generalized Boltzmann equation. The remarkable point here is that the generalized Boltzmann operator can be expressed in terms of non-connected contributions to the transport operator. This happens for the correction proportional to c^3 (c = concentration) and for the following terms in the virial expansion of the generalized Boltzmann operator.

A. The Transport Operator (Asymptotic Cross-section)

In order to calculate a transport coefficient, we can set $\Omega(i0) = 1$ in Eq. (45). We then integrate over every momentum except $\mathbf{p}_1$ and explicitly take account of the factorization of $\rho_{\{0\}}(t)$ and of the normalization of φ_1:

$$\int d\mathbf{p}_1 \varphi_1(\mathbf{p}_i, t) = 1 \tag{54}$$

which can be established starting from Eqs. (3), (7), and (14). We obtain an equation which is only valid for the study of a

transport coefficient

$$\left(\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t}\right)_{\text{collisions}} = iN^{n-1}\int d\mathbf{p}_2 \cdots \int d\mathbf{p}_n \Psi_{(0)}^{(1\cdots n)} \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i, t) \tag{55}$$

It can be verified that $\Psi_{(0)}^{(1\cdots n)}$, which is an abbreviated notation for $\Psi_{00}^{+(1\cdots n)}(0)$ and which is defined by the relations (35) and (55), must satisfy the following conditions:

Rule 1 No intermediate state $\{\mathbf{k}\} = 0$ exists. This is the dynamical irreducibility condition of the diagonal fragment.

Rule 2 Each of the particles 1,2, . . . , n are involved in $\Psi_{(0)}^{(1\cdots n)}$.

Rule 3 Starting from the left the first $\delta L^{(ij)}$ which appears must contain the particle 1 (otherwise the contribution will be null because of the integrations over the momenta); the other particle will have the index 2. For each of the particles which appear in the following $\delta L^{(kl)}$, three possibilities are envisaged:

(a) The two particles k and l have already been encountered and therefore numbered.

(b) One of the particles has not yet been encountered in $\Psi_{(0)}^{(1\cdots n)}$. We will designate it by the integer which corresponds to its order of appearance (3,4, . . . , n).

(c) None of the particles has been encountered in $\Psi_{(0)}^{(1\cdots n)}$. The prescription (b) is to apply to each of them.

We can then write for $\Psi_{(z)}^{(1\cdots n)}$ the following compact formula

$$i\Psi_{(z)}^{(1\cdots n)} = \langle 0|Q_2(z)\frac{1}{i(L_N^0 - z)}Q_3(z)\cdots\frac{1}{i(L_N^0 - z)}Q_n(z)|0\rangle' \tag{56}$$

$$\langle\{\mathbf{k}\}|Q_r(z)|\{\mathbf{k}'\}\rangle = \sum_{j=1}^{r-1}\sum_{m=0}^{\infty}\langle\{\mathbf{k}\}|(-i\lambda\delta L^{(jr)})\left(\frac{1}{i(L_N^0 - z)}(-i\lambda\delta L_r)\right)^m|\{\mathbf{k}'\}\rangle \tag{57}$$

and where L_N^0 and δL_r are defined by Eqs. (4) and (5).

In the following we will have need of the explicit expressions for the first few $\Psi^{(1\cdots n)}_{(z)}$:

$$i\Psi^{(12)}_{(z)} = \langle 0|Q_2(z)|0\rangle'$$

$$= i\sum_{m=0}^{\infty}(-\lambda)^{m+1}\langle 0|\delta L^{(12)}\left(\frac{1}{L_N^0 - z}\,\delta L^{(12)}\right)^m|0\rangle' \tag{58}$$

$$i\Psi^{(123)}_{(z)} = \langle 0|Q_2(z)\frac{1}{i(L_N^0 - z)}Q_3(z)|0\rangle'$$

$$= i\sum_{m=0}^{\infty}\sum_{m'=0}^{\infty}(-\lambda)^{m+m'+2}\langle 0|\delta L^{(12)}\left(\frac{1}{L_N^0 - z}\,\delta L^{(12)}\right)^m$$

$$\times\frac{1}{L_N^0 - z}(\delta L^{(13)} + \delta L^{(23)})$$

$$\times\left[\frac{1}{L_N^0 - z}(\delta L^{(12)} + \delta L^{(13)} + \delta L^{(23)})\right]^{m'}|0\rangle' \tag{59}$$

$$i\Psi^{(1234)}_{(z)} = \langle 0|Q_2(z)\frac{1}{i(L_N^0 - z)}Q_3(z)\frac{1}{i(L_N^0 - z)}Q_4(z)|0\rangle'$$

$$= i\sum_{m=0}^{\infty}\sum_{m'=0}^{\infty}\sum_{m''=0}^{\infty}(-\lambda)^{m+m'+m''+3}\langle 0|\delta L^{(12)}\left(\frac{1}{L_N^0 - z}\,\delta L^{(12)}\right)^m$$

$$\times\frac{1}{L_N^0 - z}(\delta L^{(13)} + \delta L^{(23)})$$

$$\times\left[\frac{1}{L_N^0 - z}(\delta L^{(12)} + \delta L^{(13)} + \delta L^{(23)})\right]^{m'}$$

$$\times\frac{1}{L_N^0 - z}(\delta L^{(14)} + \delta L^{(24)} + \delta L^{(34)})\left[\frac{1}{L_N^0 - z}\right.$$

$$\left.\times(\delta L^{(12)} + \delta L^{(13)} + \delta L^{(14)} + \delta L^{(23)} + \delta L^{(24)} + \delta L^{(34)})\right]^{m''}|0\rangle' \tag{60}$$

In expression (56) we have omitted the contributions which correspond to the rule 3c. Such terms are not possible in either $\Psi^{(12)}_{(z)}$ or $\Psi^{(123)}_{(z)}$. They only appear with $n = 4$ and for the $\Psi^{(1\cdots n)}_{(z)}$ of higher order. The omission of these terms is unimportant in

the study of the transport equation. Indeed their contribution to the asymptotic cross-section vanishes on integrating over the velocities (see Eq. 55) when one calculates $\left(\frac{\partial \varphi_1}{\partial t}\right)^{(n)}$. We shall further see that their contribution to the generalized Boltzmann equation does not vanish on integrating over the velocities. For example, the operator $\chi_{(z)}^{(12)(34)}$ defined below does not contribute to the transport equation for $(\partial \varphi_1/\partial t)^{(4)}$, but we shall show later that it is the only term of the type 3c which will give a non-zero contribution to the generalized Boltzmann equation for $n = 4$:

$$i\varepsilon_{(z)}^{(12)(34)} = i\sum_{m=0}^{\infty}(-\lambda)^{m+1}\langle 0|\delta L^{(12)}\left[\frac{1}{L_N^0 - z}(\delta L^{(12)} + \delta L^{(34)})\right]^m|0\rangle - i\Psi_{(z)}^{(12)} \quad (61)$$

$$= i\chi_{(z)}^{(12)(34)} + i\sum_{m=0}^{\infty}\sum_{m'=1}^{\infty}(-\lambda)^{m+m'+1} \times \langle 0|\delta L^{(12)}\left(\frac{1}{L_N^0 - z}\delta L^{(12)}\right)^m\left(\frac{1}{L_N^0 - z}\delta L^{(34)}\right)^{m'}|0\rangle \quad (62)$$

by definition of $\chi_{(z)}^{(12)(34)}$, which is the four-particle irreducible part of $\varepsilon_{(z)}^{(12)(34)}$.

Equation (56) merits some more comment:

(a) $\Psi_{(z)}^{(1\cdots n)}$ is written in the form of a series in λ. This expansion diverges for real forces when λ is not small (hard spheres). It will therefore be necessary to make partial summations in order to regroup the ensemble of contributions with n particles into operators which retain some meaning when the coupling parameter is arbitrary.[19,31]

(*b*) Another delicate point is the dynamical irreducibility condition which excludes those terms where all the wave vectors are zero in the same intermediate state. We shall see what this condition implies from a mathematical point of view; physically it means that those processes where some particles are momentarily separated by an infinite distance are excluded.[21]

In order to study systematically the expression (56), we shall use a very convenient technique in which each contribution to $i\Psi_{(z)}^{(1\cdots n)}$ is represented by a diagram. For reasons which will

become clear later, we shall be forced to consider not only the irreducible terms but also those for which there are intermediate states $\{\mathbf{k}\} = 0$ (reducible). Therefore, we shall not use the diagrams of Prigogine and Balescu,[15] where these states $\{\mathbf{k}\} = 0$ are not considered, but rather those which were introduced by Résibois[20] in a quantum problem and by Résibois and the author[4] in a classical one.

We shall draw a horizontal line to represent the propagation of each of the n particles. These lines are connected two by two by vertical lines which correspond to the binary interactions. To each horizontal line is associated a wave vector $\mathbf{k}_s$ ($s = 1,2, \ldots, n$) of the particle s. The wave vectors are modified by the interactions with the following selection rule:

$$\langle\{\mathbf{k}\}|\delta L^{(ij)}|\{\mathbf{k}'\}\rangle$$

$$= \frac{1}{V} V_{|\mathbf{k}_i - \mathbf{k}_{i'}|}(\mathbf{k}_i - \mathbf{k}_i') \cdot \left(\frac{\partial}{\partial \mathbf{p}_i} - \frac{\partial}{\partial \mathbf{p}_j}\right) \delta^{\mathrm{Kr}}_{\mathbf{k}_i + \mathbf{k}_j,\, \mathbf{k}_{i'} + \mathbf{k}_{j'}} \prod_{l \neq i \neq j} \delta^{\mathrm{Kr}}_{\mathbf{k}_l,\, \mathbf{k}_{l'}} \tag{63}$$

where we have set

$$V_k = \int d\mathbf{r} \exp(-i\mathbf{k} \cdot \mathbf{r}) V(r) \tag{64}$$

and

$$\begin{aligned} \delta^{\mathrm{Kr}}_{\{\mathbf{k}\},\{\mathbf{k}'\}} &= 1 \quad \text{when} \quad \{\mathbf{k}\} = \{\mathbf{k}'\} \\ &= 0 \text{ otherwise} \end{aligned} \tag{65}$$

On the other hand, the "propagators" $(L_N^o - z)^{-1}$ conserve the wave vectors

$$\langle\{\mathbf{k}\}|(L_N^0 - z)^{-1}|\{\mathbf{k}'\}\rangle = (\sum_l \mathbf{k}_l \cdot \mathbf{v}_l - z)^{-1} \delta^{\mathrm{Kr}}_{\{\mathbf{k}\},\{\mathbf{k}'\}} \tag{66}$$

Thus, each diagram represents a succession of binary interactions alternating with intermediate states where the particles are propagated freely and connects an initial state (on the right) to a final state (on the left)

For example, Fig. 2a symbolizes the following contribution with four particles:

$$i\lambda^4 \langle 0|\delta L^{(12)} \frac{1}{L_N^0 - z} \delta L^{(24)} \frac{1}{L_N^0 - z} \delta L^{(13)} \frac{1}{L_N^0 - z} \delta L^{(34)}|0\rangle \tag{67}$$

It would be useful to be able to distinguish the *connected* diagrams from the *non-connected* diagrams. In general, one can, for a given contribution, separate the particles into "clusters"

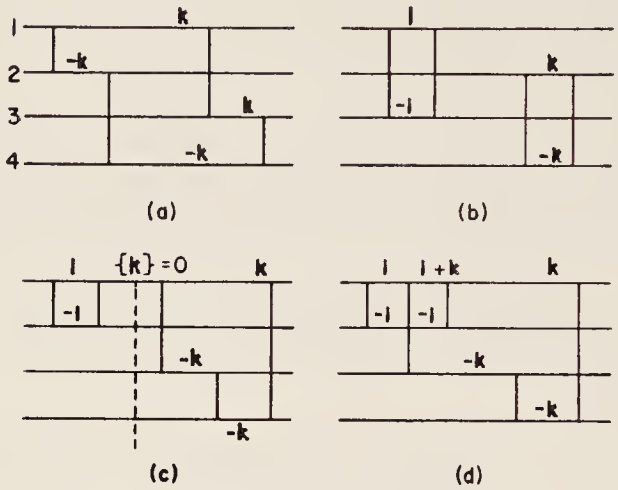


Fig. 2. Some simple diagrams.

such that each particle of each cluster interacts (in the process envisaged) only with the other particles of the same cluster. The contribution is said to be connected if $d = 1$ (Figs. 2a, c, and d) and otherwise non-connected (Fig. 2b).

Let us now consider a given contribution to $i\Psi^{(1}_{(z)}\cdots{}^{n)}$ proportional to λ^r and involving d clusters. We associate with it a diagram with $r - 1$ intermediate states. On account of the formal property of the eigenvectors

$$\sum_{\{\mathbf{k}\}} |\{\mathbf{k}\}\rangle\langle\{\mathbf{k}\}| = 1 \tag{68}$$

(see Eq. 32), such a contribution involves $n(r - 1)$ sums over the individual wave vectors $\mathbf{k}$. These sums are not all independent because each of the r $\delta L^{(ij)}$ (Eq. 63) introduces $n - 1$ conditions of the type $\delta^{\mathrm{Kr}}_{\mathbf{k},\mathbf{k}'}$ (see Eq. 65). In all, there are $r(n - 1) - d$ conditions because for each cluster one of the $\delta^{\mathrm{Kr}}_{\mathbf{k},\mathbf{k}'}$ is automatically satisfied. From this fact there remains

$$n(r - 1) - [r(n - 1) - d] = r - n + d$$

independent vectors $\mathbf{k}$ over which it is necessary to sum. For

example, for Figs. 2a and b, one has $r = n = 4$; in case a, $d = 1$ and there is one independent wave vector $\mathbf{k}$, while in case b $d = 2$ and there are two wave vectors $\mathbf{k}$ and $\mathbf{l}$. One can likewise verify the rule for Figs. 2c and d. In the limit of a large system the spectrum of $\mathbf{k}$ is continuous and

$$\sum_{\mathbf{k}} \to \frac{V}{8\pi^3} \int d\mathbf{k} \tag{69}$$

Hence, each of the $r - n + d$ sums over $\mathbf{k}$ "absorbs" one of the r factors V^{-1} introduced by the $\delta L^{(ij)}$ (see Eq. 63). We conclude from this that each diagram with d "clusters" contributing to $i\Psi_{(z)}^{(1 \cdots n)}$ is proportional to V^{d-n}. However, as is expected on the basis of the rules stated by Prigogine and Balescu,[15] only the diagrams where $d = 1$ contribute to the transport equation for $\partial\varphi_1/\partial t$; the others (non-connected) vanish in the integration over the momenta. For $d = 1$ the contribution is proportional to c^{n-1} (see Eq. 55).

Let us now specify the nature of the dynamical irreducibility condition in Eq. (56). The conservation rules of the wave vectors (Eq. 63) impose the condition that the $\mathbf{k}$ of certain particles is zero in certain intermediate states. For example, in Fig. 2a particles 2 and 3 have their $\mathbf{k}$ zero in the second state of propagation. It may be that the structure of the diagram is such that for one or many intermediate states the $\mathbf{k}$ of every particle is identically zero. The diagram is then reducible (see Fig. 2c) and is not contained in Eq. (56). This leads us to extend the definition of $i\Psi_{(z)}^{(1 \cdots n)}$ so as to include in it the reducible contributions. We shall define

$$i\bar{\Psi}_{(z)}^{(1 \cdots n)} = \langle 0 | Q_2(z) \frac{1}{i(L_N^0 - z)} Q_3(z) \cdots \frac{1}{i(L_N^0 - z)} Q_n(z) | 0 \rangle \tag{70}$$

where one has to note the disappearance of the "prime" sign on the second member.

The reducibility evidently does not change the dependence on V of the diagrams: the terms (c) and (d) (Fig. 2) are both proportional to λ^5 and both have two "free" wave vectors; they are then both proportional to V^{-2} although (c) is reducible while (d) is not. Nevertheless, in the double sum over $\mathbf{k}$ and $\mathbf{l}$

which figures in (d), one can arbitrarily select the point $\mathbf{k} = 0$ (or $\mathbf{l} = 0$) and hence obtain contributions for which, in certain states, all the $\mathbf{k}$ are null. Such terms are not called reducible. Besides, each time that one arbitrarily selects $\mathbf{k} = 0$, one introduces a $\delta^{\mathrm{Kr}}_{\kappa,0}$ and a supplementary factor V^{-1}. Such terms will then—if they are connected—include more factors V^{-1} than factors N. In the limit of a large system (26), they will be null.

It is advantageous to introduce at this stage the notion of a skeleton diagram. Every diagram where there are no two successive interactions acting on the same pair of particles is a skeleton diagram or skeleton (see Fig. 3). With any diagram

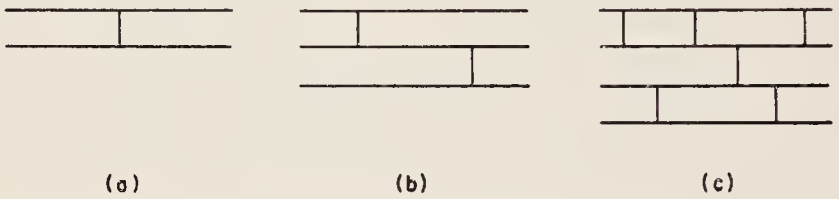
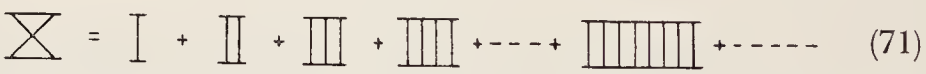


Fig. 3. Three skeletons.

whatsoever we can associate a skeleton, drawing only one vertical line for an uninterrupted sequence of interactions acting upon the same pair of particles. Reciprocally, starting from each skeleton we can easily reconstruct the class of diagrams which corresponds to it: it suffices to replace each line by an arbitrary number of lines. We shall represent the class of diagrams associated with a given skeleton by substituting a cross for each vertical line of the skeleton. Thus, the class engendered from the skeleton of Fig. 3a will be the "binary kernel":


(71)

Whatever the λ, the binary kernel gives a convergent contribution[18] to the evolution of $\varphi_1(\mathbf{p}_1, t)$. This solves, in principle at least, the problem of the divergence of the Born development (Eqs. 56, 57).

The formulation in terms of binary kernels presents another advantage: indeed, in the series (71) the selection rules (63) never impose $\mathbf{k} = 0$. The terms $\mathbf{k} = 0$ of Eq. (71) are not reducible and give negligible contributions to $(\partial\varphi_1/\partial t)^{(2)}$ (proportional to NV^{-2}). The binary kernel is therefore irreducible.

Because of this property and of the convergence of series (71), we shall treat all diagrams of the same class in the same way.

When $n > 2$, one can draw the reducible contributions made up of sequences of binary kernels and where states $\{\mathbf{k}\} = 0$ between these kernels exist. Thus, the class associated with the skeleton of Fig. 3b contains a state $\{\mathbf{k}\} = 0$ and contributes, not to Eq. (56), but to Eq. (70). In the following we shall need the relation which expresses $\Psi_{(z)}^{(1\cdots n)}$ as the difference between $\bar{\Psi}_{(z)}^{(1\cdots n)}$ and the ensemble of reducible contributions to (70) (of the type of Fig. 3b for $n = 3$, for example). It is necessary for us now to study systematically the points $\{\mathbf{k}\} = 0$ of Eq. (70) so as to extract the reducible contributions. A study of the selection rules will permit us to solve this problem. We shall associate the appearance of the points $\{\mathbf{k}\} = 0$ with the structure of the skeletons that we have introduced: we shall see that the reducibility will be a dynamical translation of certain topological properties of the equilibrium clusters.

To this end we shall associate with each contribution of Eq. (70) a connected graph[30] constructed in the following fashion: each particle is represented by a point and we connect two points by one line when the two particles considered interact one or more times in the contribution in question. In a graph there may exist an articulation point* at which time the graph can be divided

Fig. 4. Simple stars.

into two or more disconnected parts at this point. The articulation points (represented by the small circles) are the common vertices of two or more stars, which are elements (line, triangle, square traversed or not by diagonals, etc., . . .) without articulation points (see Fig. 4).

Thus, Fig. 5 represents a contribution $\bar{\Psi}_{z}^{(1\cdots 5)}$ with five particles and the graph which one associates with it in an unequivocal fashion by means of the rule which has just been presented.

* The definition adopted here for this notion is different from that which was used in Section II (1,2-irreducible graphs).

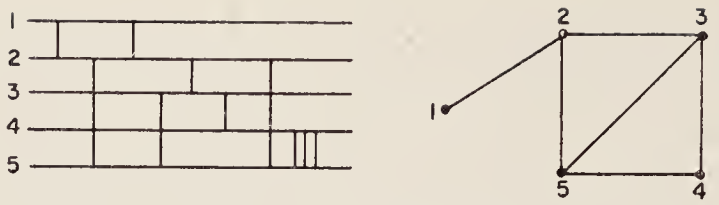


Fig. 5. A diagram and the corresponding graph.

Let us consider first a contribution such that the corresponding graph has no articulation point (see Fig. 6). Any intermediate

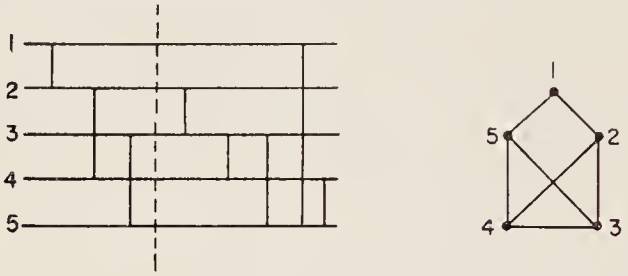


Fig. 6. An irreducible diagram and the corresponding star.

state whatsoever subdivides the particles into two sub-graphs according to which they interact before or after the given intermediate state. These two sub-graphs—owing to the absence of an articulation point—have at least two particles in common, and the selection rules which impose $\sum_i \mathbf{k}_i = 0$ can be satisfied without each of the two wave vectors being zero. The star corresponds then to an irreducible process.

Let us see now what happens when one has an articulation point (see Fig. 7a). This time the intermediate state i defines

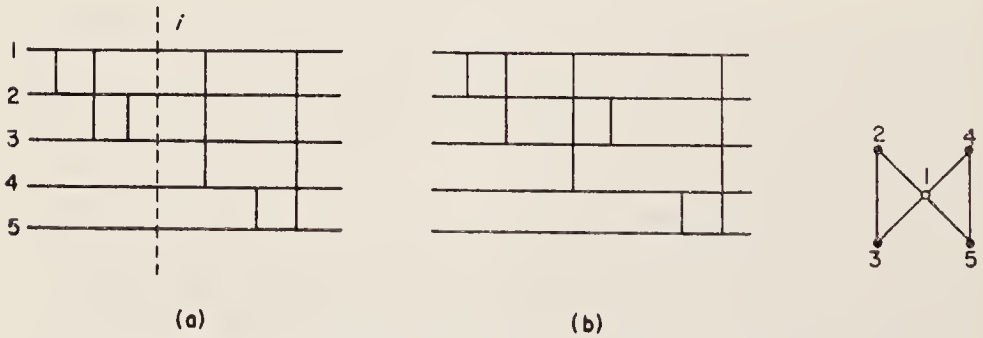
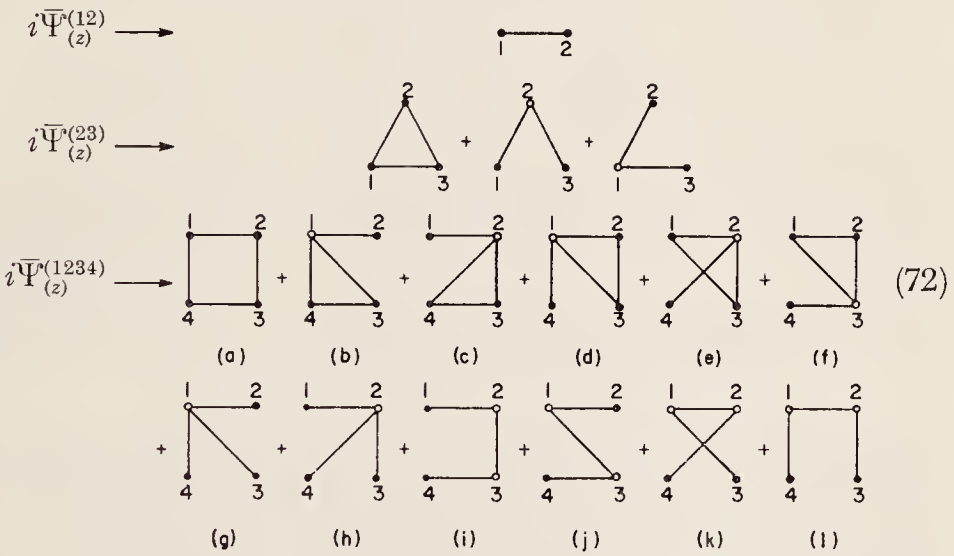


Fig. 7. Two diagrams and the corresponding graph.

two sub-graphs which have only the articulation point in common. Since the initial state is a vacuum, particles 2 and 3, which no longer interact to the right of state i, have a null wave vector in this state. The same applies to particles 4 and 5. The condition $\sum_i \mathbf{k}_i = 0$ prescribes then that the wave vector of particle 1 is also zero in the state i and the contribution is then reducible.

It is clear that two diagrams giving rise to the same graph may be reducible or not according to the order in which the interactions occur. For example, diagrams (a) and (b) of Fig. 7 are respectively reducible and irreducible even though one associates the same graph with them.

In general, a diagram whose graph contains l stars will have $l - 1$ states $\{\mathbf{k}\} = 0$ on the condition that all the stars be chronologically separated in the diagram considered. Let us then write symbolically all the graphs generated by expressions (70) (we have to remember rules 2 and 3):



(72)

Let us now use this graphical representation to extract the reducible contributions which are included in $\overline{\Psi}^{(1 \cdots n)}_{(z)}$. There are of course no such contributions for $\overline{\Psi}^{(12)}_{(z)}$, but they can be found in $\overline{\Psi}^{(123)}_{(z)}$, for which we shall now recall the result of Résibois.[23] Let us therefore write down the contributions corresponding to the second graph for $\overline{\Psi}^{(123)}_{(z)}$. We see that the interaction (1,3) between particles 1 and 3 does not appear in this graph. To get

its contributions we have only to replace $\delta L^{(13)}$ by zero in expression (70) for $\bar{\Psi}^{(123)}_{(z)}$. We obtain

$$i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} (-\lambda)^{m+m'+2} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \frac{1}{L_N^0 - z} \delta L^{(23)} \times \left[\frac{1}{L_N^0 - z} (\delta L^{(12)} + \delta L^{(23)}) \right]^{m'} | 0 \rangle$$

Since we have not yet applied the condition of chronological separation, this expression still contains irreducible contributions —those in which, starting from the left, the first $\delta L^{(23)}$ appears before the last $\delta L^{(12)}$—but they are easily eliminated so that the reducible contributions corresponding to our graph are given by the expression (see Eq. 58)

$$i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} (-\lambda)^{m+m'+2} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \times \left(\frac{1}{L_N^0 - z} \delta L^{(23)} \right)^{m'+1} | 0 \rangle = \frac{i}{(-z)} \Psi^{(12)}_{(z)} \Psi^{(23)}_{(z)}$$

From what has been said, one obtains the following relations:

$$i \bar{\Psi}^{(12)}_{(z)} = i \Psi^{(12)}_{(z)} \tag{73}$$

and

$$i \bar{\Psi}^{(123)}_{(z)} = i \Psi^{(123)}_{(z)} + \frac{i}{(-z)} \Psi^{(12)}_{(z)} [\Psi^{(13)}_{(z)} + \Psi^{(23)}_{(z)}] \tag{74}$$

The irreducible contributions to $\bar{\Psi}^{(123)}_{(z)}$ generated by the two graphs with an articulation point are included in $\Psi^{(123)}_{(z)}$, which also contains all the contributions coming from the graph with three lines. The factor $1/-z$ in Eq. (74) comes from a propagator (66) with $\{\mathbf{k}\} = 0$.

We now have to apply the same methods to $\bar{\Psi}^{(1234)}_{(z)}$. Let us first note that graph (a) represents all the contributions without articulation points (also those with more than four lines) and furnishes only irreducible terms (included in $\Psi^{(1234)}_{(z)}$). On the other hand, graph (b) contains reducible contributions. To obtain them, we again suppress in Eq. (70) the $\delta L^{(ij)}$ corresponding to the

lines which are not present in (b), i.e., (23) and (24). There remains

$$i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \times \frac{1}{L_N^0 - z} \delta L^{(13)} \left[\frac{1}{L_N^0 - z} (\delta L^{(12)} + \delta L^{(13)}) \right]^{m'} \times \frac{1}{L_N^0 - z} (\delta L^{(14)} + \delta L^{(34)}) \times \left[\frac{1}{L_N^0 - z} (\delta L^{(12)} + \delta L^{(13)} + \delta L^{(14)} + \delta L^{(34)}) \right]^{m''} | 0 \rangle$$

Moreover, the two stars must be chronologically separated so that we only keep

$$i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \times \left(\frac{1}{L_N^0 - z} \delta L^{(13)} \right)^{m'+1} \frac{1}{L_N^0 - z} (\delta L^{(14)} + \delta L^{(34)}) \times \left[\frac{1}{L_N^0 - z} (\delta L^{(13)} + \delta L^{(14)} + \delta L^{(34)}) \right]^{m''} | 0 \rangle$$

We are sure that each term of this expression contains at least one interaction (12) and one interaction (13). However, it is easy to write the terms where (14) or (34) is absent. These have to be subtracted because they do not correspond to the graph (b). Doing this, we get all the reducible contributions arising from this graph, which can be written

$$\text{(b)} = i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \times \left(\frac{1}{L_N^0 - z} \delta L^{(13)} \right)^{m'+1} \frac{1}{L_N^0 - z} \times \Bigg\{ (\delta L^{(14)} + \delta L^{(34)}) \left[\frac{1}{L_N^0 - z} (\delta L^{(13)} + \delta L^{(14)} + \delta L^{(34)}) \right]^{m''} - \delta L^{(14)} \left[\frac{1}{L_N^0 - z} (\delta L^{(13)} + \delta L^{(14)}) \right]^{m''} - \delta L^{(34)} \left[\frac{1}{L_N^0 - z} (\delta L^{(13)} + \delta L^{(34)}) \right]^{m''} \Bigg\} | 0 \rangle$$

By using the relations (70) for $(1, \ldots, n) = (134)$ and (74) we obtain

$$\begin{aligned}(\mathrm{b}) + (\mathrm{c}) = {} & \frac{i}{(-z)} \Psi'^{(12)}_{(z)} \{\Psi'^{(134)}_{(z)} + \Psi'^{(234)}_{(z)}\} \\ & - \frac{i}{(-z)} \Psi'^{(12)}_{(z)} \{\varepsilon^{(13)(14)}_{(z)} + \varepsilon^{(13)(34)}_{(z)} + \varepsilon^{(23)(24)}_{(z)} + \varepsilon^{(23)(34)}_{(z)}\} \\ & + \frac{i}{(-z)^2} \Psi'^{(12)}_{(z)} \{\Psi'^{(13)}_{(z)} (\Psi'^{(14)}_{(z)} + \Psi'^{(34)}_{(z)}) + \Psi'^{(23)}_{(z)} (\Psi'^{(24)}_{(z)} + \Psi'^{(34)}_{(z)})\} \end{aligned} \tag{75}$$

The quantity $\varepsilon^{(13)(14)}_{(z)}$ is defined in complete analogy with $\varepsilon^{(12)(34)}_{(z)}$ (see Eq. (61)) and is easily written:

$$\begin{aligned} i\varepsilon^{(13)(14)}_{(z)} = {} & i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} (-\lambda)^{m+m'+2} \langle 0 | \delta L^{(13)} \left(\frac{1}{L^0_N - z} \delta L^{(13)} \right)^m \\ & \times \frac{1}{L^0_N - z} \delta L^{(14)} \left[\frac{1}{L^0_N - z} (\delta L^{(13)} + \delta L^{(14)}) \right]^{m'} | 0 \rangle \end{aligned} \tag{76}$$

The same procedure can be applied to graphs (d), (e), and (f), and the reducible contributions associated with them are

$$\begin{aligned} (\mathrm{d}) + (\mathrm{e}) + (\mathrm{f}) = {} & \frac{i}{(-z)} \Psi'^{(123)}_{(z)} \{\Psi'^{(14)}_{(z)} + \Psi'^{(24)}_{(z)} + \Psi'^{(34)}_{(z)}\} \\ & - \frac{i}{(-z)} \{\varepsilon^{(12)(13)}_{(z)} + \varepsilon^{(12)(23)}_{(z)}\} \{\Psi'^{(14)}_{(z)} + \Psi'^{(24)}_{(z)} + \Psi'^{(34)}_{(z)}\} \\ & + \frac{i}{(-z)^2} \Psi'^{(12)}_{(z)} \{\Psi'^{(13)}_{(z)} + \Psi'^{(23)}_{(z)}\} \{\Psi'^{(14)}_{(z)} + \Psi'^{(24)}_{(z)} + \Psi'^{(34)}_{(z)}\} \end{aligned} \tag{77}$$

Finally, we look for the reducible contributions of one of the graphs with three stars. For example, graph (l), where the lines (13), (24), and (34) do not appear, corresponds, in Eq. (70), to the class of terms

$$\begin{aligned} & i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \langle 0 | \delta L^{(12)} \left(\frac{1}{L^0_N - z} \delta L^{(12)} \right)^m \\ & \quad \times \frac{1}{L^0_N - z} \delta L^{(23)} \left[\frac{1}{L^0_N - z} (\delta L^{(12)} + \delta L^{(23)}) \right]^{m'} \\ & \quad \times \frac{1}{L^0_N - z} \delta L^{(14)} \left[\frac{1}{L^0_N - z} (\delta L^{(12)} + \delta L^{(23)} + \delta L^{(14)}) \right]^{m''} | 0 \rangle \end{aligned}$$

It is easy to write down the reducible contributions which this expression contains

$$
\begin{aligned}
(\mathrm{l}) = i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \\
\times \left(\frac{1}{L_N^0 - z} \delta L^{(23)} \right)^{m'+1} \left(\frac{1}{L_N^0 - z} \delta L^{(14)} \right)^{m''+1} | 0 \rangle \\
+ i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \\
\times \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \frac{1}{L_N^0 - z} \delta L^{(23)} \\
\times \left\{ \left[\frac{1}{L_N^0 - z} (\delta L^{(12)} + \delta L^{(23)}) \right]^{m'} \right. \\
\left. - \left(\frac{1}{L_N^0 - z} \delta L^{(23)} \right)^{m'} \right\} \\
\times \left(\frac{1}{L_N^0 - z} \delta L^{(14)} \right)^{m''+1} | 0 \rangle \\
+ i \sum_{m=0}^{\infty} \sum_{m'=0}^{\infty} \sum_{m''=0}^{\infty} (-\lambda)^{m+m'+m''+3} \langle 0 | \delta L^{(12)} \left(\frac{1}{L_N^0 - z} \delta L^{(12)} \right)^m \\
\times \left(\frac{1}{L_N^0 - z} \delta L^{(23)} \right)^{m'+1} \frac{1}{L_N^0 - z} \delta L^{(14)} \\
\times \left\{ \left[\frac{1}{L_N^0 - z} (\delta L^{(23)} + \delta L^{(14)}) \right]^{m''} - \left(\frac{1}{L_N^0 - z} \delta L^{(14)} \right)^{m''} \right\} | 0 \rangle
\end{aligned}
$$

The first term corresponds to the contributions with two $\{\mathbf{k}\} = 0$ points where the three stars are chronologically separated from each other. In the second one, the star (14) is chronologically separated from (12) and (23), which are, however, mixed. In the third term, (12) is separated from the mixed stars (23) and (14). The two last terms contain only one $\{\mathbf{k}\} = 0$ point. Using Eqs. (58) and (76) we obtain:

$$
\begin{aligned}
(\mathrm{l}) = \frac{i}{(-z^2)} \Psi_{(z)}^{(12)} \Psi_{(z)}^{(23)} \Psi_{(z)}^{(14)} + \frac{i}{(-z)} \left\{ \varepsilon_{(z)}^{(12)(23)} - \frac{1}{(-z)} \Psi_{(z)}^{(12)} \Psi_{(z)}^{(23)} \right\} \psi_{(z)}^{(14)} \\
+ \frac{i}{(-z)} \Psi_{(z)}^{(12)} \left\{ \varepsilon_{(z)}^{(23)(14)} - \frac{1}{(-z)} \Psi_{(z)}^{(23)} \Psi_{(z)}^{(14)} \right\} \qquad (78)
\end{aligned}
$$

It is easy to extend the same procedure to the graphs (g), (h), (i), (j), and (k) to obtain

$$\begin{aligned}(g) + (h) + (i) + (j) + (k) + (l) = &- \frac{i}{(-z)^2}\,\Psi^{\prime(12)}_{(z)}[\Psi^{\prime(13)}_{(z)} + \Psi^{\prime(23)}_{(z)}] \\ &\times [\Psi^{\prime(14)}_{(z)} + \Psi^{\prime(24)}_{(z)} + \Psi^{\prime(34)}_{(z)}] + \frac{i}{(-z)}\,[\varepsilon^{(12)(13)}_{(z)} + \varepsilon^{(12)(23)}_{(z)}] \\ &\times [\Psi^{\prime(14)}_{(z)} + \Psi^{\prime(24)}_{(z)} + \Psi^{\prime(34)}_{(z)}] + \frac{i}{(-z)}\,\Psi^{\prime(12)}_{(z)} \\ &\times [\varepsilon^{(13)(14)}_{(z)} + \varepsilon^{(13)(24)}_{(z)} + \varepsilon^{(13)(34)}_{(z)} + \varepsilon^{(23)(14)}_{(z)} + \varepsilon^{(23)(24)}_{(z)} + \varepsilon^{(23)(34)}_{(z)}]\end{aligned} \tag{79}$$

Now we are able to obtain an expression for the difference between $\bar{\Psi}^{(1234)}_{(z)}$ and $\Psi^{(1234)}_{(z)}$: it is the sum of all the contributions (75), (77), and (79), so that we can write (see also Eq. 62)·

$$\begin{aligned}i\bar{\Psi}^{(1234)}_{(z)} = i\Psi^{(1234)}_{(z)} &+ \frac{i}{(-z)}\,\Psi^{\prime(12)}_{(z)}[\Psi^{\prime(134)}_{(z)} + \Psi^{\prime(234)}_{(z)}] \\ &+ \frac{i}{(-z)}\,\Psi^{\prime(123)}_{(z)}[\Psi^{\prime(14)}_{(z)} + \Psi^{\prime(24)}_{(z)} + \Psi^{\prime(34)}_{(z)}] \\ &+ \frac{i}{(-z)^2}\,\Psi^{\prime(12)}[\Psi^{\prime(13)}_{(z)} + \Psi^{\prime(23)}_{(z)}][\Psi^{\prime(14)}_{(z)} + \Psi^{\prime(24)}_{(z)} + \Psi^{\prime(34)}_{(z)}] \\ &+ \frac{i}{(-z)}\,\Psi^{\prime(12)}_{(z)}[\chi^{(13)(24)}_{(z)} + \chi^{(23)(14)}_{(z)}]\end{aligned} \tag{80}$$

Let us now multiply the two members of Eqs. (74) and (80) by $(1/2\pi iz)\exp(-iz\tau)$, integrate over the variable z along the contour C (see Fig. 1), and pass finally to the limit $\tau \to \infty$. We obtain:

$$\begin{aligned}\lim_{\tau\to\infty} iF^{(123)}_{(\tau)} = \lim_{\tau\to\infty} \{&i\Psi^{\prime(123)}_{(0)} - i[\Psi^{\prime(12)}_{(z)}(\Psi^{\prime(13)}_{(z)} + \Psi^{\prime(23)}_{(z)})]'_{z=0} \\ &-i(-i\tau)\Psi^{\prime(12)}_{(0)}[\Psi^{\prime(13)}_{(0)} + \Psi^{\prime(23)}_{(0)}]\}\end{aligned} \tag{81}$$

$$\lim_{\tau\to\infty} iF^{(1234)}_{(\tau)} = \lim_{\tau\to\infty}\{i\Psi^{(1234)}_{(0)} - i[\Psi^{(12)}_{(z)}(\Psi^{(134)}_{(z)} + \Psi^{(234)}_{(z)})$$
$$+ \Psi^{(123)}_{(z)}(\Psi^{(14)}_{(z)} + \Psi^{(24)}_{(z)} + \Psi^{(34)}_{(z)})]'_{z=0}$$
$$-i(-i\tau)[\Psi^{(12)}_{(0)}(\Psi^{(134)}_{(0)} + \Psi^{(234)}_{(0)}) + \Psi^{(123)}_{(0)}(\Psi^{(14)}_{(0)} + \Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)})]$$
$$+ \frac{i}{2}[(-i\tau)^2\Gamma_{(0)} + 2(-i\tau)\Gamma'_{(0)} + \Gamma''_{(0)}]$$
$$+ i(-i\tau)^2\Psi^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)}$$
$$+ i(-i\tau)[2\Psi'^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)} + \Psi^{(12)}_{(0)}(\Psi^{(13)}_{(z)}\Psi^{(24)}_{(z)})'_{z=0}]$$
$$+ i\Psi''^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)} + i\Psi'^{(12)}_{(0)}\Psi'^{(13)}_{(0)}\Psi^{(24)}_{(0)}$$
$$+ i\Psi'^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi'^{(24)}_{(0)} + i\Psi^{(12)}_{(0)}\Psi'^{(13)}_{(0)}\Psi'^{(24)}_{(0)}\} \tag{82}$$

We have closed the contour C by means of a semicircle of infinite radius in the lower half plane. The integrand is zero on this half circle because τ is positive. In the closed contour thus obtained, we have applied the residue theorem. The only contributions to be retained come from the poles at $z = 0$; indeed, the poles of the operators $\Psi^{(1\cdots n)}_{(z)}$ are situated in the lower half plane and give terms affected by an exponential which vanishes for $\tau \to \infty$.

We have used the following notations:

$$F^{(1\cdots n)}_{(\tau)} = \frac{1}{2\pi i}\int_C \frac{dz}{z}\exp(-iz\tau)\bar{\Psi}^{(1\cdots n)}_{(z)} \tag{83}$$

and

$$\Gamma_{(z)} = \Psi^{(12)}_{(z)}[\Psi^{(13)}_{(z)}\{\Psi^{(14)}_{(z)} + \Psi^{(34)}_{(z)}\} + \Psi^{(23)}_{(z)}\{\Psi^{(24)}_{(z)} + \Psi^{(34)}_{(z)}\}] \tag{84}$$

Finally, it is necessary to remark that the operators $\chi^{(ij)(kl)}_{(z)}$ which appeared in Eq. (80) have been expressed in terms of the operators $\Psi^{(ij)}_{(z)}$ and their derivatives taken at $z = 0$. This transformation has been effected by means of a factorization theorem.[22] The details of the calculation appear in Appendix A.1.

B. The Generalized Boltzmann Operator

We start from Eq. (45) which describes the evolution of $\rho_{\{0\}}(t)$ for long times. We look for the contributions to $\partial\varphi_1/\partial t$ and we

proceed in the same manner as in obtaining Eq. (55):

$$\left(\frac{\partial\varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(n)} = iN^{n-1}\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n (\Omega(i0)\Psi^{+}_{00}(i0))^{(1\ldots n)} \times \prod_{j=1}^{n} \varphi_1(\mathbf{p}_j, t) \quad (85)$$

If we make explicit the relations (46) and (47), we obtain

$$\Omega_0(i0) = 1$$

$$\Omega_1(i0) = -\left[\frac{\partial}{\partial z}\Psi^{+}_{00}(z)\right]_{z=i0} = -\Psi'^{(12)}_{(0)} - \Psi'^{(123)}_{(0)} - \ldots$$

$$\Omega_2(i0) = \frac{1}{2}\left[\frac{\partial^2}{\partial z^2}\Psi^{+}_{00}(z)\right]_{z=i0}\Psi^{+}_{00}(i0) + \left[\frac{\partial\Psi^{+}_{00}(z)}{\partial z}\right]_{z=i0}\left[\frac{\partial\Psi^{+}_{00}(z)}{\partial z}\right]_{z=i0}$$

$$= \tfrac{1}{2}\Psi''^{(12)}_{(0)}[\Psi^{(13)}_{(0)} + \Psi^{(23)}_{(0)}] + \Psi'^{(12)}_{(0)}[\Psi'^{(13)}_{(0)} + \Psi'^{(23)}_{(0)}] + \ldots \quad (86)$$

In these expressions we have classified the terms according to their dependence on V^{-1}. This is not modified by the derivatives which act on the $\Psi^{(1\ldots n)}_{(z)}$ as $\partial\Psi^{(1\ldots n)}_{(z)}/\partial z \simeq \tau_c\Psi^{(1\ldots n)}_{(z)}$ One can, consequently, apply the rule $\Psi^{(1\ldots n)}_{(z)} \simeq V^{d-n}$. In order to number the particles, we have also to take into account rule 3 which follows Eq. (55).

Let us also remark that the only products of the $\Psi^{(1\ldots n)}_{(z)}$ and their derivatives which will appear in Eq. (85) will correspond to graphs with a single cluster. Otherwise, the contribution to Eq. (85) of the corresponding product $\Omega\Psi$ will be null by integration over the momenta.

We have limited ourselves in Eq. (86) to the terms in V^0, V^{-1}, and V^{-2}. This is justified in as far as we limit Eq. (85) to the contributions proportional to c^3; indeed the terms in V^{-3} in Ω must still be multiplied by Ψ (whose dominant term is V^{-1}) and would thus give in Eq. (85) contributions proportional to c^4.

In order to calculate $\Omega\Psi$, let us now multiply $\Omega(i0)$ by $\Psi^{+}_{00}(i0)$, which we write:

$$\Psi^{+}_{00}(i0) = \Sigma\Psi^{(ij)}_{(0)} + \Sigma\Psi^{(ijk)}_{(0)} + \Sigma\Psi^{(ijkl)}_{(0)} + \Sigma\chi^{(ij)(kl)}_{(0)} \quad (87)$$

where the summations are over the indices of the particles. The terms $\Psi^{(1\cdots n)}_{(0)}$ are given by Eqs. (56) and (57) and therefore do not contain terms of the type 3c. The contributions of type 3c may be connected or non-connected and evidently contain at least four particles.

(a) If they are connected, they are of order V^{-p}, where $p \geqslant 3$. Since we shall always limit ourselves to the order c^3 in Eq. (85), the connected contributions 3c can only be multiplied by the only term in V^0 of Eq. (86), that is 1. Consequently, the connected terms of the type 3c are again annuled by the integration over the momenta in Eq. (86) (on condition that terms in c^4, c^5, . . . , etc., are neglected).

(b) If they are non-connected they can be proportional to V^{-2} and one can then find a contribution to $\Omega\Psi$ in V^{-3}; it suffices to multiply the only term in V^{-1} in Eq. (86) (let it be $\Psi'^{(12)}_{(0)}$) by $\chi^{(13)(24)}_{(0)} + \chi^{(23)(14)}_{(0)}$, which is the only term of the type 3c in Eq. (87) which will furnish a non-zero contribution and be proportional to c^3 in Eq. (85).

Let us now multiply expression (86) by (87); then we obtain without difficulty:

$$[\Omega(i0)\Psi^{+}_{00}(i0)]^{(12)} = \Psi^{(12)}_{(0)} \tag{88}$$

$$[\Omega(i0)\Psi^{+}_{00}(i0)]^{(123)} = \Psi^{(123)}_{(0)} - \Psi'^{(12)}_{(0)}[\Psi^{(13)}_{(0)} + \Psi^{(23)}_{(0)}] \tag{89}$$

$$\begin{aligned}[\Omega(i0)\Psi^{+}_{00}(i0)]^{(1234)} = {} & \Psi^{(1234)}_{(0)} - \Psi'^{(123)}_{(0)}[\Psi^{(14)}_{(0)} + \Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)}] \\ & - \Psi'^{(12)}_{(0)}[\Psi^{(134)}_{(0)} + \Psi^{(234)}_{(0)} + \chi^{(13)(24)}_{(0)} + \chi^{(23)(14)}_{(0)}] \\ & + \tfrac{1}{2}\Psi''^{(12)}_{(0)}[\Psi^{(13)}_{(0)} + \Psi^{(23)}_{(0)}][\Psi^{(14)}_{(0)} + \Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)}] \\ & + \Psi'^{(12)}_{(0)}[\Psi'^{(13)}_{(0)} + \Psi'^{(23)}_{(0)}][\Psi^{(14)}_{(0)} + \Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)}]\end{aligned} \tag{90}$$

There remains one non-trivial step to take: that is to calculate the $\chi^{(ij)(kl)}_{(0)}$ from expression (90) in terms of the $\Psi^{(ij)}_{(0)}$ and their derivatives. To this end, we have again used the factorization theorem which has recently been demonstrated by Résibois.[22] In order not to destroy the continuity of the exposition we shall

give the details of the calculations in Appendix A.II, where we establish that Eq. (90) can be written as:

$$
\begin{aligned}
&[\Omega(i0)\Psi^{+}_{00}(i0)]^{(1234)} \\
&= \Psi^{(1234)}_{(0)} - \Psi'^{(123)}_{(0)}[\Psi^{(14)}_{(0)} + \Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)}] - \Psi'^{(12)}_{(0)}[\Psi^{(134)}_{(0)} + \Psi^{(234)}_{(0)}] \\
&\quad + \tfrac{1}{2}\Psi''^{(12)}_{(0)}[\Psi^{(13)}_{(0)} + \Psi^{(23)}_{(0)}][\Psi^{(14)}_{(0)} + \Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)}] \\
&\quad + \Psi'^{(12)}_{(0)}[\Psi'^{(13)}_{(0)}(\Psi^{(14)}_{(0)} + \Psi^{(34)}_{(0)}) + \Psi'^{(23)}_{(0)}(\Psi^{(24)}_{(0)} + \Psi^{(34)}_{(0)})] \qquad (91)
\end{aligned}
$$

From expressions (88), (89), and (91) one easily verifies that $[\Omega(i0)\Psi^{+}_{00}(i0)]^{(1\cdots n)}$ is proportional to V^{-n+1}; consequently Eq. (85) constitutes the series expansion in the concentration of $\partial\varphi_1/\partial t$.

V. EQUIVALENCE BETWEEN THE STREAMING OPERATORS METHOD AND PRIGOGINE'S THEORY

We are now able to bring to a successful conclusion the comparison between the results of Bogolubov,[3] Choh and Uhlenbeck,[6] and Cohen[8] and the theory of Prigogine.[14] That is the object of this section. For the case of dilute gases, we shall rapidly redemonstrate the equivalence between the result of Cohen[8] and that of Prigogine.[14] Then we shall concern ourselves with the virial corrections to the generalized Boltzmann equation. We recall the work of Stecki *et al.* who expanded the results of Bogolubov[3] in a series in λ[28] and showed[29] that this expansion is identical to all orders in λ with the generalized Boltzmann operator in the Prigogine version.[17] For the first virial correction we expound the work of Résibois,[21,23] who established the identity between Cohen's results[8] and those of Prigogine.[14] We use this method to demonstrate, to the same order in c, the equivalence between the expressions of Choh and Uhlenbeck[6] and the generalized Boltzmann equation in the Prigogine formalism.[14] For the next correction in c, we establish the equivalence between the formula of Cohen[8] and that of Prigogine.[14]

Finally, we calculate the transport operator for three particles in the Cohen formalism. We obtain, evidently, an expression which differs from that for the generalized Boltzmann operator in the same formalism.

In conclusion, we expound the principles which might serve

as a basis for the extension of these proofs to all orders in c: the remarkable structure of Cohen's expressions in Fourier space, on the one hand, and, on the other hand, the simple relation between the appearance of reducible contributions and the existence, in the corresponding equilibrium graphs, of articulation points.

A. Generalities and the Dilute Gas Case

We shall demonstrate explicitly the equivalence between the results of Bogolubov, Choh and Uhlenbeck, and Cohen (BCUC) and the generalized Boltzmann equation in Prigogine's theory. But it seems useful to us to indicate beforehand some qualitative arguments which allow a physical understanding of the grounds on which this equivalence rests (for more details see ref. 24).

(a) The results that we shall like to compare are only valid for times sufficiently far removed from the initial instant. Indeed, Bogolubov's fundamental hypothesis is not justified before the kinetic stage is reached and the generalized Boltzmann equation (45) is the long-time limit in Prigogine's theory.

(b) The two theories are valid for a very large class of initial conditions; however, both make the hypothesis that the initial correlations are of finite range. This is, in effect, the physical content of the boundary conditions (9) imposed by Bogolubov (see, for example, ref. 3). It is also this hypothesis which allows one to neglect the destruction fragment in Prigogine's theory (see Eq. 40) and to obtain the generalized Boltzmann equation (45).

In the dilute gas case, we can easily establish the equivalence between the results of BCUC and Prigogine's theory.

Let us start by writing Cohen's results (24) in wave vector space. We obtain

$$\left(\frac{\partial \varphi_1(\mathbf{p}_1, t)}{\partial t}\right)^{(n)} = c^{n-1} V^{n-1} \lim_{\tau \to \infty} \int d\mathbf{p}_2 \cdots \int d\mathbf{p}_n \times \langle 0 | B_{-\tau}^{(1 \cdots n)} | 0 \rangle \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i, t) \quad (92)$$

Let us also define the Laplace transform of the streaming operator (10) (see Fig. 1)

$$S_{-t}^{(1 \cdots n)} = -\frac{1}{2\pi i} \int_G dz S_{(z)}^{(1 \cdots n)} \exp(-izt) \quad (93)$$

It is easy to show that

$$S_z^{(1\ldots n)} = \frac{1}{L_n - z} \tag{94}$$

and from this one gets for $n = 2$ (since in this case the irreducibility condition does not play any role):

$$\langle 0|\theta_{12}S_{(z)}^{(12)}|0\rangle = -i\Psi_{(z)}^{(12)}/z \tag{95}$$

Let us now substitute this expression in Eq. (93) where we pass to the limit $t \to \infty$. Since $t > 0$, let us close the contour C by means of a large semicircle in the lower half plane and apply the residue theorem. The result is

$$\lim_{t\to\infty} \langle 0|\theta_{12}S_{-t}^{(12)}|0\rangle = i\Psi_{(0)}^{(12)} \tag{96}$$

because the contributions of the poles of $\Psi_{(z)}^{(12)}$ are affected by an exponential which tends towards zero for $t \to \infty$.

If this expression is substituted in Eqs. (25) and (92), we obtain exactly the $n = 2$ term of the generalized Boltzmann equation (see Eqs. 85 and 88) as it appears in the Prigogine formalism. This result is thus equivalent to the formulae (24) and (25) of Cohen's theory from which we started.

This is evidently nothing new. Indeed, for a dilute gas, the equations of evolution for the distribution function for one particle derived by Bogolubov, Prigogine and Cohen have been identified with the original result of Boltzmann (see, respectively, refs. 3, 16, and 8).

B. The Dense Gas Case: Contributions for Three Particles

Let us mention first the work of Stecki who expanded Bogolubov's results in a series in λ[28] and who with Taylor showed that this expansion is identical to all orders in λ with the generalized Boltzmann operator (85).[29] Since the method is rather different from the virial expansions which we present here, we give in Appendix A.III the major thoughts of this general work valid for any concentration.

As far as the concentration version is concerned, Résibois has studied Cohen's results[21,23] and has established the equivalence

between the collision term for three particles obtained by this author[8] and the generalized Boltzmann operator for $n = 3$ in the Prigogine formalism (Eqs. 85 and 89).

We shall first recollect the demonstration by Résibois (Section VB-1) and then use his method and demonstrate the equivalence between:

(1) Choh and Uhlenbeck's result and the generalized Boltzmann operator for $n = 3$ in the Prigogine formalism (Section VB-2).

(2) The collision term for four particles in Cohen's version and the general Boltzmann operator for $n = 4$ in the Prigogine formalism (Section VC).

(1) *Equivalence between* $\langle 0|\theta_{12}B^{(123)}_{-\tau}|0\rangle$ *and* $[\Omega(i0)\Psi^{+}_{00}(i0)]^{(123)}$

Let us begin by writing $\langle 0|\theta_{12}B^{(123)}_{-\tau}|0\rangle$ explicitly in wave vector space. Starting from Eq. (25) and taking into account the conservation rules for the wave vectors (Eq. 63), we see that the intermediate state between the two-particle streaming operators is $\{\mathbf{k}\} = 0$, which gives:

$$\langle 0|\theta_{12}B^{(123)}_{-\tau}|0\rangle = \langle 0|\theta_{12}S^{(123)}_{-\tau}|0\rangle - \langle 0|\theta_{12}S^{(12)}_{-\tau}|0\rangle \times [\langle 0|S^{(13)}_{-\tau}|0\rangle + \langle 0|S^{(23)}_{-\tau}|0\rangle - 1] \quad (97)$$

By a trivial but somewhat long calculation, we can establish the following relations (see Eqs. 59, 70, 93, and 94):

$$\langle 0|\theta_{12}S^{(123)}_{-\tau}|0\rangle = -\frac{1}{2\pi i}\int_C dz\,\frac{-i}{z}\,[\bar{\Psi}^{(123)}_{(z)} + \Psi'^{(12)}_{(z)}]\exp(-iz\tau) \quad (98)$$

and

$$\langle 0|S^{(13)}_{-\tau}|0\rangle = -\frac{1}{2\pi i}\int_C dz\left[-\frac{1}{z} + \frac{1}{z^2}\Psi'^{(13)}_{(z)}\right]\exp(-iz\tau) \quad (99)$$

We can at present close the contour C and apply the residue theorem, which gives (see Eq. 83):

$$\lim_{\tau\to\infty}\langle 0|\theta_{12}S^{(123)}_{-\tau}|0\rangle = \lim_{\tau\to\infty} i\{F^{(123)}_{(\tau)} + \Psi'^{(12)}_{(0)}\} \quad (100)$$

and

$$\lim_{\tau\to\infty}\langle 0|S^{(13)}_{\tau-}|0\rangle = \lim_{\tau\to\infty}\{1 - \Psi'^{(13)}_{(0)} - (-i\tau)\Psi'^{(13)}_{(0)}\} \quad (101)$$

Equations (96), (97), (100), and (101) allow us to write

$$\lim_{\tau\to\infty}\langle 0|\theta_{12}B^{(123)}_{-\tau}|0\rangle =$$

$$\lim_{\tau\to\infty}[iF^{(123)}_{(\tau)} + i\Psi'^{(12)}_{(0)}\{\Psi'^{(13)}_{(0)} + \Psi'^{(23)}_{(0)} + (-i\tau)(\Psi'^{(13)}_{(0)} + \Psi'^{(23)}_{(0)})\}] \tag{102}$$

and if we take into account relation (81) we obtain

$$\lim_{\tau\to\infty}\langle 0|\theta_{12}B^{(123)}_{-\tau}|0\rangle = i[\Psi'^{(123)}_{(0)} - \Psi'^{(12)}_{(0)}(\Psi'^{(13)}_{(0)} + \Psi'^{(23)}_{(0)})]$$

$$= i[\Omega(i0)\Psi'^{+}_{00}(i0)]^{(123)} \tag{103}$$

by virtue of expression (89). By substituting this result in Eq. (92) we obtain expression (85), which allows us to conclude that the Cohen formalism and the Prigogine theory give identical results for $n = 3$.

(2) *Equivalence between* $\langle 0|\theta_{12}A^{(123)}_{-\tau}|0\rangle$ *and* $[\Omega(i0)\Psi'^{+}_{00}(i0)]^{(123)}$

The operator (12) obtained by Choh and Uhlenbeck[6] can be decomposed in the following fashion:

$$A^{(123)}_{-\tau} = \alpha^{(1)}_{-\tau} + \alpha^{(2)}_{-\tau} - \beta^{(1)}_{-\tau} - \beta^{(2)}_{-\tau} \tag{104}$$

where we have set

$$\alpha^{(1)}_{-\tau} = \theta_{12}\int_0^\infty dt' S^{(12)}_{-t'}\theta_{13}S^{(123)}_{-\tau} \tag{105}$$

and

$$\beta^{(1)}_{-\tau} = \theta_{12}\int_0^\infty dt' S^{(12)}_{-t'}S^{(12)}_{-\tau}\theta_{13}S^{(13)}_{-\tau} \tag{106}$$

and $\alpha^{(2)}_{-\tau}$ and $\beta^{(2)}_{-\tau}$ are given by expressions (105) and (106) but with the index 1 replaced by 2 and vice versa.

It is clear that

$$\lim_{\tau\to\infty}\langle 0|\beta^{(1)}_{-\tau}|0\rangle = \lim_{\tau\to\infty}\tau\langle 0|\theta_{12}S^{(12)}_{-\tau}\theta_{13}S^{(13)}_{-\tau}|0\rangle \tag{107}$$

because the streaming operator (10) has the following property

$$S^{(1\ldots n)}_{t+t'} = S^{(1\ldots n)}_{t}S^{(1\ldots n)}_{t'} \tag{108}$$

By using Eq. (93), we obtain:

$$\lim_{\tau\to\infty}\langle 0|\beta^{(1)}_{-\tau}|0\rangle = \lim_{\tau\to\infty}\left(-\frac{1}{2\pi i}\right)^2\tau\int_C dz\int_C dz'\exp\left[-i(z+z')\tau\right] \times\langle 0|\theta_{12}S^{(12)}_{(z)}|0\rangle\langle 0|\theta_{13}S^{(13)}_{(z')}|0\rangle \quad (109)$$

and finally, because of Eqs. (95) and (96), we can write

$$\lim_{\tau\to\infty}\langle 0|\beta^{(1)}_{-\tau}|0\rangle = -\lim_{\tau\to\infty}\tau\Psi'^{(12)}_{(0)}\Psi^{(13)}_{(0)} \quad (110)$$

Let us consider now the term $\alpha^{(1)}_{-\tau}$ in Eq. (104). By the definition of the $\sigma(z)$, we can write (see Eq. 93)

$$\lim_{\tau\to\infty}\langle 0|\alpha^{(1)}_{-\tau}|0\rangle = \lim_{\tau\to\infty}\left(-\frac{1}{2\pi i}\right)^2\int_C dz\int_C dz'\frac{\exp(-iz'\tau)(\exp(-iz\tau)-1)}{-iz} \times\left\{\langle 0|\theta_{12}S^{(12)}_{(z)}|0\rangle\langle 0|\theta_{13}S^{(13)}_{(z')}|0\rangle + \left(\frac{1}{-z'}\right)\langle 0|\theta_{12}S^{(12)}_{(z)}\theta_{13}(\sigma^{(123)}_{(z')}-\sigma^{(13)}_{(z')})|0\rangle\right\} \quad (111)$$

We have written the first term, which corresponds to the only reducible contribution of $\alpha^{(1)}_{-\tau}$, separately and, moreover, we have made the poles which are not located in the lower half plane appear explicitly in the integrand.

Let us now perform the integrations over z and z'. The term which does not contain an exponential $\exp(-iz\tau)$ does not contribute because we can complete the contour C by a semicircle in the upper half plane where the integrand has no poles. By using Eq. (96), we obtain:

$$\lim_{\tau\to\infty}\langle 0|\alpha^{(1)}_{-\tau}+\alpha^{(2)}_{-\tau}|0\rangle = -i\lim_{\tau\to\infty}[\Psi'^{(12)}_{(0)}-i\tau\Psi^{(12)}_{(0)}][\Psi^{(13)}_{(0)}+\Psi^{(23)}_{(0)}] + \frac{1}{i}\lim_{\tau\to\infty}\langle 0|\theta_{12}S^{(12)}_{(0)}[(\theta_{13}+\theta_{23})\sigma^{(123)}_{(0)}-\theta_{13}\sigma^{(13)}_{(0)}-\theta_{23}\sigma^{(23)}_{(0)}]|0\rangle \quad (112)$$

Now, we can easily verify that

$$\langle 0|\theta_{12}S^{(12)}_{(z)}[(\theta_{13}+\theta_{23})\sigma^{(123)}_{(z)}-\theta_{13}\sigma^{(13)}_{(z)}-\theta_{23}\sigma^{(23)}_{(z)}]|0\rangle = -\Psi'^{(123)}_{(z)} \quad (113)$$

and, by combining relations (104), (110), (112), and (113), we can write

$$\lim_{\tau\to\infty}\langle 0|A_{-\tau}^{(123)}|0\rangle = i[\Psi_{(0)}^{(123)} - \Psi'^{(12)}_{(0)}(\Psi_{(0)}^{(13)} + \Psi_{(0)}^{(23)})]$$
$$= i[\Omega(i0)\Psi_{00}^{+}(i0)]^{(123)} \qquad (114)$$

On the other hand, the evolution equations derived by Choh and Uhlenbeck (Eqs. 11 and 12) can be written in the wave vector space (see Eq. 92 with $n = 3$ and where $B_{-\tau}^{(123)}$ is replaced by $A_{-\tau}^{(123)}$). Consequently, expression (114) establishes the equivalence between the result of Choh and Uhlenbeck (Eqs. 11 and 12) and the generalized Boltzmann equation in the Prigogine formalism (see Eq. (85)).

C. The Dense Gas Case: Contributions for Four Particles

We should like to demonstrate the equivalence between the Cohen result (see Eq. 92 for $n = 4$) and the generalized Boltzmann equation (see Eq. 85 for $n = 4$) in the Prigogine formalism.

To do this we must study the structure of the operator $\langle 0|B_{-\tau}^{(1234)}|0\rangle$ given by expression (25″). This appears as a sum of products of the operators $S_{-\tau}^{(1;\cdots s)}$ preceded from the left by an operator θ_{12}. It is necessary to remark that for each of the terms and for every pair of operators $S_{-\tau}^{(1;\cdots s)}$, never more than one particle is repeated. These particles common to two $S_{-\tau}^{(1;\cdots s)}$ will be articulation points in the graph language defined above and, consequently, all the intermediate states between the operators $S_{-\tau}^{(1;\cdots s)}$ will be $\{\mathbf{k}\} = 0$. Furthermore, this remark is general and valid to all orders in the concentration in Cohen's formalism.

Hence, the only quantities which appear in Cohen's results will be $\langle 0|S_{-\tau}^{(1;\cdots s)}|0\rangle$ and $\langle 0|\theta_{12}S_{-\tau}^{(1;\cdots s)}|0\rangle$ in the limit $\tau\to\infty$. We shall now write down the relations between these quantities and the $\Psi_{(0)}^{(1;\cdots s)}$ defined previously.

By comparing relations (70), (74), and (94) we establish that

$$\langle 0|S_{(z)}^{(134)}|0\rangle = -\frac{1}{z} + \frac{2}{z^2}[\bar{\Psi}_{(z)}^{(134)} + \Psi_{(z)}^{(13)}]$$
$$= -\frac{1}{z} + \frac{2}{z^2}[\Psi_{(z)}^{(134)} + \Psi_{(z)}^{(13)} - \frac{1}{z}\Psi_{(z)}^{(13)}(\Psi_{(z)}^{(14)} + \Psi_{(z)}^{(34)})] \qquad (115)$$

from which we obtain, by applying formula (93),

$$\lim_{\tau\to\infty}\langle 0|S^{(134)}_{-\tau}|0\rangle = \lim_{\tau\to\infty}\{1 - 2[\Psi'^{(134)}_{(0)} + \Psi'^{(13)}_{(0)}] - 2(-i\tau)[\Psi^{(134)}_{(0)} + \Psi^{(13)}_{(0)}] + (-i\tau)^2 E_{134}(0) + 2(-i\tau)E'_{134}(0) + E''_{134}(0)\} \quad (116)$$

where by definition

$$E_{134}(z) = \Psi^{(13)}_{(z)}\{\Psi^{(14)}_{(z)} + \Psi^{(34)}_{(z)}\} \quad (117)$$

In the same way we can demonstrate the following relation:

$$\langle 0|\theta_{12}S^{(1234)}_{(z)}|0\rangle = -\frac{i}{z}[2\bar{\Psi}^{(1234)}_{(z)} + 2\bar{\Psi}^{(123)}_{(z)} + \Psi^{(12)}_{(z)}] \quad (118)$$

and, from this, by recalling the definition (83), establish that

$$\lim_{\tau\to\infty}\langle 0|\theta_{12}S^{(1234)}_{-\tau}|0\rangle = i\lim_{\tau\to\infty}[2F^{(1234)}_{(\tau)} + 2F^{(123)}_{(\tau)} + \Psi^{(12)}_{(0)}] \quad (119)$$

The remainder of the calculation is elementary but somewhat long. One can proceed in the following way: in expression (25″) one inserts the results (96), (100), (101), (116), (117), and (119). One then obtains with no difficulty an equation in which the operator $\langle 0|B^{(1234)}_{-\tau}|0\rangle$ is expressed in terms of $F^{(123)}_{(\tau)}$, $F^{(1234)}_{(\tau)}$ and the $\Psi^{(1\cdots s)}_{(0)}$ for 2 and 3 particles, as well as their derivatives also evaluated at $z = 0$. This expression is valid for $\tau \to \infty$. We do not write it explicitly because it is very lengthy, yet elementary to obtain. The final stage consists in eliminating the operators $F^{(123)}_{(\tau)}$ and $F^{(1234)}_{(\tau)}$ which still appear in the result. This is performed by means of Eqs. (81), (82), and (84). The result is then considerably simplified. In particular, the divergent terms in the limit $\tau \to \infty$ compensate each other exactly, as they must do. Finally, we obtain (see Eq. 91):

$$\lim_{\tau\to\infty}\langle 0|B^{(1234)}_{-\tau}|0\rangle = i[\Omega(i0)\Psi^{+}_{00}(i0)]^{(1234)} \quad (120)$$

If one puts this result in the expression (92) which proceeds from Cohen's results, one retrieves the equation (85) of the Prigogine theory. This establishes the equivalence between these two methods of formulating the generalization of the Boltzmann equation for the collisions of four particles.

D. The Transport Operator in the Streaming Operators Formalism

We should now like to express the transport operator for three particles in terms of the streaming operators. We start from expression (74) and we use relation (95) to obtain:

$$i\Psi^{(123)}_{(z)} = i\bar{\Psi}^{(123)}_{(z)} - iz\langle 0|\theta_{12}S^{(12)}_{(z)}|0\rangle \times [\langle 0|\theta_{13}S^{(13)}_{(z)}|0\rangle + \langle 0|\theta_{23}S^{(23)}_{(z)}|0\rangle] \quad (121)$$

Let us multiply each member by $\exp(-iz\tau)/2\pi iz$, integrate over z along the contour C (see Fig. 1) and pass to the limit $\tau \to \infty$. The first member is obtained by the same type of argument as that which leads to Eq. (81). The first term on the right-hand side of the above equation is calculated by means of relations (83), (96), and (100), which give

$$\lim_{\tau\to\infty} \frac{1}{2\pi i}\int_G dz \frac{i}{z}\bar{\Psi}^{(123)}_{(z)} \exp(-iz\tau) = \lim_{\tau\to\infty}\{\langle 0|\theta_{12}S^{(123)}_{-\tau}|0\rangle - \langle 0|\theta_{12}S^{(12)}_{-\tau}|0\rangle\} \quad (122)$$

The last two terms of Eq. (121) are evaluated by observing that they are products of Laplace transforms. By applying the convolution theorem, we obtain

$$-\lim_{\tau\to\infty}\frac{1}{2\pi i}\int_C dz\,\langle 0|\theta_{12}S^{(12)}_{(z)}|0\rangle\langle 0|\theta_{13}S^{(13)}_{(z)}|0\rangle \exp(-iz\tau) = i\lim_{\tau\to\infty}\int_0^\tau d\tau'\langle 0|\theta_{12}S^{(12)}_{-\tau+\tau'}|0\rangle\langle 0|\theta_{13}S^{(13)}_{-\tau'}|0\rangle \quad (123)$$

Let us combine the results (122) and (123), whereby we obtain

$$i\Psi^{(123)}_{(0)} = \lim_{\tau\to\infty}\Big\{\langle 0|\theta_{12}S^{(123)}_{-\tau}|0\rangle - \langle 0|\theta_{12}S^{(12)}_{-\tau}|0\rangle - \int_0^\tau d\tau'\,\langle 0|\theta_{12}S^{(12)}_{-\tau+\tau'}|0\rangle[\langle 0|\theta_{13}S^{(13)}_{-\tau'}|0\rangle + \langle 0|\theta_{23}S^{(23)}_{-\tau'}|0\rangle]\Big\} \quad (124)$$

which is the classical analogue of the quantum result recently obtained by Résibois.[25]

Equation (124) gives an expression for the transport operator

in the Cohen formalism.[8] This quantity must not be confused with the generalized Boltzmann operator, which is written in the same formalism (see Eqs. 25′ and 97) as

$$i[\Omega(i0)\Psi^{+}_{00}(i0)]^{(123)} = \lim_{\tau\to\infty}\{\langle 0|\theta_{12}S^{(123)}_{-\tau}|0\rangle + \langle 0|\theta_{12}S^{(12)}_{-\tau}|0\rangle - \langle 0|\theta_{12}S^{(12)}_{-\tau}|0\rangle[\langle 0|S^{(13)}_{-\tau}|0\rangle + \langle 0|S^{(23)}_{-\tau}|0\rangle]\} \quad (125)$$

Just as we reported in Section III, the transport coefficients are determined by Eq. (124). This does not mean that one would not be able to evaluate such quantities by means of an expression in which the operator (125) figured explicitly (see Severne[27]). His procedure is equivalent to multiplying formally both members of Eq. (55) by the operator $\Omega(i0)$.

E. Conclusions

We have also studied the generalized Boltzmann operator for four particles in the Choh–Uhlenbeck formalism (see, for example, this expression in the work of Cohen[8]). Since the paper by Stecki and Taylor,[29] it seems clear that the results of Bogolubov and those of Choh and Uhlenbeck (which are derived from them) must be equivalent to the Prigogine formalism. However, it is very difficult to show this equivalence explicitly in the concentration form that we have presented here. Indeed, in the Choh and Uhlenbeck method, the streaming operators appear with their Fourier components $\langle\{\mathbf{k}\}|S^{(1}_{-\tau}\cdots{}^{n)}|\{\mathbf{k}'\}\rangle$ and $\langle\{\mathbf{k}\}|\theta_{ij}S^{(1}_{-\tau}\cdots{}^{n)}|\{\mathbf{k}'\}\rangle$, and the products of these operators are then expressed in terms of the $\Psi^{(1\cdots n')}$ for several complex variables. This renders the mathematical operations extremely complicated (see Eq. 111).

On the other hand, the method that has just been employed is very advantageous for manipulating the expressions of Cohen where everything is expressed in terms of the Fourier components $\langle 0|S^{(1}_{-\tau}\cdots{}^{n)}|0\rangle$ and $\langle 0|\theta_{12}S^{(1}_{-\tau}\cdots{}^{n)}|0\rangle$ which are directly related to the operators $\Psi^{(1}_{(z)}\cdots{}^{n')}$ for one complex variable z and evaluated at $z = 0$. This simplification is considerable and it also occurs when one calculates the operators $\mathscr{V}^{(1}_{-\tau}\cdots{}^{n)}$ in Eq. (21) in terms of the operators $\mathscr{U}^{(1}_{-\tau}\cdots{}^{n')}$, where $n \geqslant n'$: while the quantity $\langle 0|B^{(1}_{-\tau}\cdots{}^{n)}|0\rangle$ contains all the Fourier components of the $\mathscr{V}^{(1}_{-\tau}\cdots{}^{n')}$, it is expressed only with the aid of the Fourier components $\langle 0|\theta_{12}\mathscr{U}^{(1}_{-\tau}\cdots{}^{n')}|0\rangle$ and $\langle 0|\mathscr{U}^{(1}_{-\tau}\cdots{}^{n')}|0\rangle$ of the operators

$\mathscr{U}^{(1}_{-\tau}\cdots{}^{n')}$. This very important property seems difficult to establish in complete generality, but the fact that it may be verified for $n \leqslant 4$ leads us to think that it is true for all values of n.

However, the operators $\langle 0|\theta_{12}S^{(1}_{-\tau}\cdots{}^{n)}|0\rangle$ $(n \geqslant 3)$ and $\langle 0|S^{(1}_{-\tau}\cdots{}^{n)}|0\rangle$ diverge in the limit where τ tends towards infinity, just as in the expressions (81), (82), (100), (101), (116), and (119). However, the great advantage of the Prigogine formalism is the elimination from the beginning of the divergent contributions due to the dynamical irreducibility condition (see Eq. 55, rule 1) and the expression of everything in terms of the operators $\Psi^{(1}_{(0)}\cdots{}^{n')}$, which remain finite. With regard to the generalized Boltzmann operators in Cohen's formalism, they are evidently finite because of the compensation of the divergent terms of which we have spoken above. In fact, these divergences are due to the configurations where the particles that have interacted are infinitely separated and then interact again. In Prigogine's theory, these configurations are eliminated by the dynamical irreducibility condition. In the formalism of Cohen they appear explicitly, and, thereby, the passage to the limit where τ tends towards infinity is particularly crucial when one wants to compare both types of results (see also note on p. 381).

Another remarkable point is the appearance in $[\Omega(i0)\Psi^{+}_{00}(i0)]^{(1\cdots n)}$ of contributions to $\Psi^{+}_{00}(i0)$ which are non-connected and that play no role in the isolated $\Psi^{+}_{00}(i0)$. These non-connected terms are present for the first time when $n = 4$ (we cannot have two $\delta L^{(ij)}$ with no particle in common if we do not have at least four particles), but also exist to higher orders in the concentration. Their evaluation necessitates some delicate mathematical manipulations (application of the factorization theorem) but the extension of this technique to the higher-order terms of the virial expansion does not seem to pose any new problem.

The fact that, as just indicated, $\langle 0|B^{(1}_{-\tau}\cdots{}^{n)}|0\rangle$ can be expressed in terms of the $\langle 0|\theta_{12}S^{(1}_{-\tau}\cdots{}^{n')}|0\rangle$ and the $\langle 0|S^{(1}_{-\tau}\cdots{}^{n')}|0\rangle$ and, finally, the remarkable relation between the appearance of the states $\{\mathbf{k}\} = 0$ and the existence of articulation points, must be the basis of the generalization to all orders of the comparison that we have presented.

However, it may be noted that a very compact proof of the equivalence between Cohen's and Prigogine's results has been

obtained very recently by P. Résibois and the author.[4a] This demonstration is valid for any concentration but, as it is less explicit than that presented above and follows a very different method, it is reported only in Appendix A.IV.

VI. APPENDICES

A.I. The Demonstration of Eq. (82)

In order to pass from Eq. (80) to Eq. (82) we must establish that (see the expressions (58) and (62))

$$
\begin{aligned}
&-\lim_{\tau\to\infty}\frac{1}{2\pi i}\int_C dz\,\exp(-iz\tau)\,\frac{\Psi^{(12)}_{(z)}}{z^2}\left[\varepsilon^{(13)(24)}_{(z)}+\varepsilon^{(23)(14)}_{(z)}\right]\\
&\quad=(-i\tau)^2\Psi^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)}+(-i\tau)\left[2\Psi'^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)}+\right.\\
&\qquad\left.\Psi^{(12)}_{(0)}\left\{\Psi^{(13)}_{(0)}\Psi^{(24)}_{(z)}\right\}'_{z=0}\right]\\
&\qquad+\Psi''^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)}+\Psi'^{(12)}_{(0)}\Psi'^{(13)}_{(0)}\Psi^{(24)}_{(0)}+\Psi'^{(12)}_{(0)}\Psi^{(13)}_{(0)}\Psi'^{(24)}_{(0}\\
&\qquad+\Psi^{(12)}_{(0)}\Psi'^{(13)}_{(0)}\Psi'^{(24)}_{(0)} \qquad\text{(A.1)}\\
&\quad=i\int_0^\infty d\tau\,\tilde{\varepsilon}(\tau) \qquad\text{(A.2)}
\end{aligned}
$$

where $\tilde{\varepsilon}(\tau)$ is the Laplace transform

$$
\tilde{\varepsilon}(\tau)=-\frac{1}{2\pi i}\int_C dz\,\exp(-iz\tau)\left\{-\frac{\psi^{(12)}_{(z)}}{z}\left[\varepsilon^{(13)(24)}_{(z)}+\varepsilon^{(23)(14)}_{(z)}\right]\right\} \qquad\text{(A.3)}
$$

We apply the factorization theorem,[22] which allows us to write:

$$
\begin{aligned}
\tilde{\varepsilon}(\tau)=&\sum_{n=0}^{\infty}\sum_{l=1}^{\infty}\sum_{k=0}^{\infty}\left(\frac{\lambda}{i}\right)^{n+l+k+2}\int_0^{\tau}d\tau_1\cdots\int_0^{\tau_{n-1}}d\tau_n\int_0^{\tau_n}d\tau_{n+1}\cdots\\
&\times\int_0^{\tau_{n+l-1}}d\tau_{n+l}\int_0^{\tau_n}d\tau_{n+l+1}\cdots\int_0^{\tau_{n+l+k-1}}d\tau_{n+l+k}\\
&\times\left[\langle 0|\delta L^{(12)}(\tau)\delta L^{(12)}(\tau_1)\cdots\delta L^{(12)}(\tau_n)\delta L^{(13)}(\tau_{n+1})\cdots\right.\\
&\times\left.\delta L^{(13)}(\tau_{n+l})\delta L^{(24)}(\tau_{n+l+1})\cdots\delta L^{(24)}(\tau_{n+l+k})\delta L^{24}(0)|0\rangle\right.\\
&\left.+\text{ another term symmetrical with respect to the permutation 1,2}\right] \qquad\text{(A.4)}
\end{aligned}
$$

where

$$\delta L^{(ij)}(\tau) = \exp(iL_0\tau)\delta L^{(ij)} \exp(-iL_0\tau) \tag{A.5}$$

It is clear from the integration limits in Eq. (A.4) that the sequence of interactions between particles 1 and 2 must precede the interactions of the other types. Moreover, the expression (A.4) corresponds to the ensemble of contributions where the interactions between particles 1 and 3 are arbitrarily ordered with respect to interactions between particles 2 and 4 and it follows from the fact that the group (1,3) ignores the group (2,4) during the interval that extends from the initial instant to the instant τ_n. One can easily verify that this chronological ordering of the events is already contained in formula (A.3) (see the definition (61) of $\varepsilon_{(z)}^{(12)(34)}$).

In Eq. (A.4), the convolution products that appear are the inverted Laplace transforms of the operators $\Psi_{(z)}^{(ij)}$ and we get the results:

$$i\int_0^\infty d\tau\, \tilde{\varepsilon}(\tau) = \lim_{\tau'\to\infty}\left(-\frac{1}{2\pi i}\right)^3 \int_\gamma dz \int_{\gamma_1} dz_1 \int_{\gamma_2} dz_2 \frac{\exp(-iz\tau')\Psi_{(z)}^{(12)}}{z(z_1+z_2-z)} \times \left[\frac{\Psi_{(z_1)}^{(13)}\Psi_{(z_2)}^{(24)}}{z_1^2 z_2} + \frac{\Psi_{(z_2)}^{(23)}\Psi_{(z_1)}^{(14)}}{z_2^2 z_1}\right] \tag{A.6}$$

where the contours γ_1, γ_2, and γ are represented in Fig. 8. Permuting particles 3 and 4 in the second term of this expression, we obtain

$$i\int_0^\infty d\tau\, \tilde{\varepsilon}(\tau) = \lim_{\tau'\to\infty}\left(-\frac{1}{2\pi i}\right)^3 \int_\gamma dz \int_{\gamma_1} dz_1 \int_{\gamma_2} dz_2 \times \frac{\exp(-iz\tau')\Psi_{(z)}^{(12)}\Psi_{(z_1)}^{(13)}\Psi_{(z_2)}^{(24)})}{zz_1^2 z_2^2(z_1+z_2-z)} \{(z_1+z_2-z)+z\} \tag{A.7}$$

The brackets contain two terms: the first (between parentheses) gives zero. Indeed, since the variables z_1, z_2, and z in it are independent we have the right to close the contours corresponding to z_1 or z_2 in the upper half plane and we do not then include any poles. The other term must be treated in detail.

Let us integrate first over z. The only pole which contributes is $z = z_1 + z_2$ on the condition that $Im(z_1 + z_2) < 2a$. We obtain

$$i\int_0^\infty d\tau\, \tilde{\varepsilon}(\tau) = \lim_{\tau'\to\infty}\left(\frac{1}{2\pi i}\right)^2 \int_{\gamma_1} dz_1 \int_{\gamma_2} dz_2 \frac{\exp\,(-i(z_1+z_2)\tau')}{z_1^2 z_2^2} \times \Psi^{(12)}_{(z_1+z_2)}\Psi^{(13)}_{(z_1)}\Psi^{(24)}_{(z_2)} \quad \text{(A.8)}$$

Let us then integrate over z_2. We close γ_2 below, which satisfies the condition mentioned above. There are three types of pole in the contour:

(a) $z_2 = 0$,

(b) z_2 in the lower half plane at $z_2 = z_2^{(i)}$,

(c) $z_1 + z_2$ in the lower half plane (do not contribute).

The poles of the type (c) do not contribute. Indeed, they give contributions proportional to exp $-i(z_1 + z_2{}^{(i)})\tau'$ so that it is

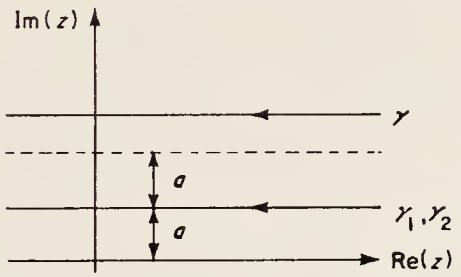


Fig. 8. The contours γ_1, γ_2, and γ.

still necessary to integrate over z_1. This integration in turn gives residues either at $z_1 = 0$, or at z_1 in the lower half plane, or lastly at $z_1 + z_2^{(i)}$ in the lower half plane. In all three cases we obtain an exponential which is annuled when τ' tends towards infinity. The poles of type (a) give

$$i\int_0^\infty d\tau\, \tilde{\varepsilon}(\tau) = \lim_{\tau'\to\infty}\left(\frac{1}{2\pi i}\right)\int_{\gamma_1} dz_1 \frac{\exp\,(-iz_1\tau')}{z_1^2} \times \{-i\tau'\Psi^{(12)}_{(z_1)}\Psi^{(13)}_{(z_1)}\Psi^{(24)}_{(0)} + \Psi'^{(12)}_{(z_1)}\Psi^{(13)}_{(z_1)}\Psi^{(24)}_{(0)} + \Psi^{(12)}_{(z_1)}\Psi^{(13)}_{(z_1)}\Psi'^{(24)}_{(0)}\} \quad \text{(A.9)}$$

Finally, one can integrate over z_1. Only $z_1 = 0$ contributes, and it is clear that we indeed obtain the proposition under the form (A.1) and (A.2).

A.II. The Demonstration of Eq. (91)

We must calculate $\chi_{(0)}^{(13)(24)}$ and we remark, first, that

$$\chi_{(z)}^{(13)(24)} = \varepsilon_{(z)}^{(13)(24)} + \frac{1}{z}\Psi_{(z)}^{(13)}\Psi_{(z)}^{(24)} \tag{A.10}$$

by virtue of the relations (58) and (62). Since $\chi_{(z)}^{(13)(24)}$ has poles only in the lower half plane, we can write

$$\begin{aligned}\chi_{(0)}^{(13)(24)} &= \lim_{\tau\to\infty}\frac{1}{2\pi i}\int_C dz\,\frac{\exp(-iz\tau)}{z}\,\chi_{(z)}^{(13)(24)} \\ &= \lim_{\tau\to\infty}\frac{1}{2\pi i}\int_C dz\,\frac{\exp(-iz\tau)-1}{z}\,\chi_{(z)}^{(13)(24)}\end{aligned} \tag{A.11}$$

because the term independent of the time does not contribute. We also have

$$\chi_{(0)}^{(13)(24)} = \lim_{\tau\to\infty}(-i)\frac{1}{2\pi i}\int_C dz\int_0^\tau d\tau'\exp(-iz\tau') \times\left[\varepsilon_{(z)}^{(13)(24)} + \frac{1}{z}\Psi_{(z)}^{(13)}\Psi_{(z)}^{(24)}\right] \tag{A.12}$$

Let us set

$$-\frac{1}{2\pi i}\int_C dz\exp(-iz\tau')\varepsilon_{(z)}^{(13)(24)} = \tilde{\varepsilon}_{(\tau')}^{(13)(24)} \tag{A.13}$$

which is the Laplace transform of $\varepsilon_{(z)}^{(13)(24)}$. By again applying the factorization theorem, we can write

$$\begin{aligned}\tilde{\varepsilon}_{(\tau')}^{(13)(24)} + \tilde{\varepsilon}_{(\tau')}^{(23)(14)} = \sum_{n=1}^{\infty}\sum_{l=1}^{\infty}\int_0^{\tau'}d\tau_1\int_0^{\tau_1}d\tau_2\cdots\int_0^{\tau_{n-1}}d\tau_n \\ \times\int_0^{\tau'}d\tau_{n+1}\cdots\int_0^{\tau_{n+l-1}}d\tau_{n+l} \\ \times\left\{\left(\frac{\lambda}{i}\right)^{n+l+2}\langle 0|\delta L^{(13)}(\tau')\delta L^{(13)}(\tau_1)\cdots\delta L^{(13)}(\tau_n)\delta L^{(24)}(\tau_{n+1}) \right. \\ \left. \cdots\delta L^{(24)}(\tau_{n+l})\delta L^{(24)}(0)|0\rangle\right\} \\ + \text{the term symmetrical with respect to the permutation 1,2}\end{aligned} \tag{A.14}$$

We remark that $\Psi^{(ij)}_{(z)}$ is the Laplace transform of each convolution product in (A.14). The expressions (A.12), (A.13), and (A.14) give then (see Fig. 8):

$$\chi^{(13)(24)}_{(0)} + \chi^{(23)(14)}_{(0)} = \lim_{\tau\to\infty} -\left(\frac{1}{2\pi i}\right)^2 \int_{\gamma_1} dz_1 \int_{\gamma_2} dz_2 \frac{\exp\left(-i(z_1+z_2)\tau\right)}{z_1 z_2 (z_1+z_2)}$$
$$\times \left[\Psi^{(13)}_{(z_1)}\psi^{(24)}_{(z_2)} + \Psi^{(23)}_{(z_1)}\psi^{(14)}_{(z_2)}\right] + \lim_{\tau\to\infty} \frac{1}{2\pi i} \int_{\gamma} dz \frac{\exp\left(-iz\tau\right)}{z^2}$$
$$\times \left[\Psi^{(13)}_{(z)}\psi^{(24)}_{(z)} + \Psi^{(23)}_{(z)}\psi^{(14)}_{(z)}\right] \tag{A.15}$$

We then perform the integrations that appear in this expression. The integration over z is trivial: only $z = 0$ contributes. We then integrate over z_2: only $z_2 = 0$ contributes. Lastly, we integrate over z_1 and finally obtain the result:

$$\chi^{(13)(24)}_{(0)} + \chi^{(23)(14)}_{(0)} = -\lim_{\tau\to\infty} \left[\Psi'^{(13)}_{(0)}\Psi^{(24)}_{(0)} + \Psi'^{(23)}_{(0)}\Psi^{(14)}_{(0)}\right.$$
$$\left. - i\tau(\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)} + \Psi^{(23)}_{(0)}\Psi^{(14)}_{(0)})\right]$$
$$+ \lim_{\tau\to\infty} \left[\{\Psi^{(13)}_{(z)}\Psi^{(24)}_{(z)} + \Psi^{(23)}_{(z)}\Psi^{(14)}_{(z)}\}'_{z=0} - i\tau(\Psi^{(13)}_{(0)}\Psi^{(24)}_{(0)} + \Psi^{(23)}_{(0)}\Psi^{(14)}_{(0)})\right]$$
$$= \Psi^{(13)}_{(0)}\Psi'^{(24)}_{(0)} + \Psi^{(23)}_{(0)}\Psi'^{(14)}_{(0)} \tag{A.16}$$

This expression, put into Eq. (90), indeed gives Eq. (91).

A.III. The Equivalence between the Theories of Bogolubov and Prigogine in the λ-Version

Bogolubov's[3] results have been expanded in a series in the coupling parameter λ by Stecki.[28] The author establishes that the term in λ^n of the expansion

$$F_s(\mathbf{x}_1, \ldots, \mathbf{x}_s, t) = \sum_{m=0}^{\infty} \lambda^m F_s^m \tag{A.17}$$

of the distribution function for s particles (see Eq. 7)

$$F_s = c^{-s} f_s = F_s(\{s\}) \tag{A.18}$$

can be put in the form

$$F_s^n = \sum_{l=0}^{n-1} c^l \mathcal{F}_s^{nl}(\{s\}) \prod_{j\in\{s\}} F_1(j) \prod_{\alpha_i\in\{l\}} F_1(\alpha_i) \tag{A.19}$$

The operators $\mathscr{T}_s^{nl}$ (written Ω_s^{nl} in the original work) are defined by the following system of recurrence relations:

$$\mathscr{T}_s^{1,0}(\{s\}) = -iP_s\delta L_s \tag{A.20}$$

$$\mathscr{T}_s^{n,0}(\{s\}) = -iP_s\delta L_s\mathscr{T}_s^{n-1,0}(\{s\}) \tag{A.21}$$

$$\mathscr{T}_s^{n,n-1}(\{s\}) = P_s\sum_{i\epsilon\{s\}}\int d\mathbf{x}_\alpha\theta_{i\alpha}[\mathscr{T}_{s+1}^{n-1,n-2}(\{s\},\alpha) - \mathscr{T}_2^{n-1,n-2}(i,\alpha)] \tag{A.22}$$

and, for $1 \leqslant l \leqslant n-2$

$$\mathscr{T}_s^{n,l}(\{s\}) = P_s\Big\{-i\delta L_s\mathscr{T}_s^{n-1,l}(\{s\}) + \sum_{i\epsilon\{s\}}\int d\mathbf{x}_\alpha\theta_{i\alpha} \times [\mathscr{T}_{s+1}^{n-1,l-1}(\{s\},\alpha) - \mathscr{T}_2^{n-1,l-1}(i,\alpha)] - \sum_{m'\geqslant 1}\sum_{m''\geqslant 1}\sum_{\nu'=0}^{m'-1}\sum_{\nu''=0}^{m''-1} \times \delta^{\mathrm{Kr}}_{m'+m'',n-1}\delta^{\mathrm{Kr}}_{\nu'+\nu'',l-1}\mathscr{T}_s^{m'\nu'}(\{s\})\Big[\sum_{i\epsilon\{s\}} + \sum_{i\epsilon\{\nu'\}}\Big]\int d\mathbf{x}_\alpha\theta_{i\alpha}\mathscr{T}_2^{m''\nu''}(i,\alpha)\Big\} \tag{A.23}$$

It is clear that the integrations over $\mathbf{x}_\alpha$ which appear in Eqs. (A.22) and (A.23) must be performed after having introduced these two expressions into (A.19). We have set

$$P_s = \int_0^\infty dt\, e^{-iL_s^0 t} \tag{A.24}$$

On the other hand, Stecki and Taylor[29] study the equation which gives the correlations in the Prigogine theory. The property (44) for the creation operator allows us to develop $\rho_{\{0\}}(t-t')$ about $t'=0$ in Eq. (48), which gives

$$\rho_{\{\mathbf{k}\}}(t\to\infty) = \hat{O}(\{\mathbf{k}\})\rho_{\{0\}}(t\to\infty) \tag{A.25}$$

with (see Eq. 45)

$$\hat{O}(\{\mathbf{k}\}) = C^+_{\{\mathbf{k}\}0}(i0) + \sum_{\nu=1}^\infty \frac{i^\nu}{\nu!}\left(\frac{\partial^\nu C^+_{\{\mathbf{k}\}0}(z)}{\partial z^\nu}\right)_{z=i0}(i\Omega(i0)\Psi^+_{00}(i0))^\nu \tag{A.26}$$

The operator $\hat{O}$ is then expanded in a series in λ

$$\hat{O}(\{\mathbf{k}\}) = \sum_{n=1}^\infty \lambda^n\hat{O}_n(\{\mathbf{k}\}) \tag{A.27}$$

and the authors use the relation

$$\left(\frac{\partial^\nu C_n^+(z)}{\partial z^\nu}\right)_{z=i0} = -iP_N\delta L_N\left(\frac{\partial^\nu C_{n-1}^+(z)}{\partial z^\nu}\right)_{z=i0} + \nu\, P_N\left(\frac{\partial^{\nu-1}C_n^+(z)}{\partial z^{\nu-1}}\right)_{z=i0} \tag{A.28}$$

($C_m^+(z)$ is the term in λ^m of Eq. (36) where the wave vectors in subscript have been omitted) in order to demonstrate a recurrence relation that $\hat{O}_m$ must in its turn satisfy

$$\hat{O}_m(\{\mathbf{k}\}) = -iP_N\delta L_N\hat{O}_{m-1}(\{\mathbf{k}\}) - P_N\sum_{l=2}^{m-1}\hat{O}_{m-l}(\{\mathbf{k}\})[i\Omega(i0)\Psi_{00}^+(i0)]_l \tag{A.29}$$

(where $[A]_l$ represents the term in λ^l of the operator A).

Stecki and Taylor also remark that the master equation (40) (where one neglects the destruction fragment) can be expanded in a series about $t' = 0$ and can be then put in the form:

$$\frac{\partial\rho_{\{0\}}(t)}{\partial t} = i\Psi_{00}^+(i0)\rho_{\{0\}}(t) + \sum_{\nu=1}^{\infty}\frac{1}{\nu!}\left(\frac{\partial^\nu\Psi_{00}^+(z)}{\partial z^\nu}\right)_{z=i0}(i\Omega(i0)\Psi_{00}^+(i0))^\nu\rho_{\{0\}}(t) \tag{A.30}$$

By comparing the relations (A.25), (A.26), and (A.30), they obtain

$$\frac{\partial\rho_{\{0\}}(t)}{\partial t} = -\lambda i\sum_{\{\mathbf{k}\}}\langle 0|\delta L_N|\{\mathbf{k}\}\rangle\rho_{\{\mathbf{k}\}}(t\to\infty) \tag{A.31}$$

because (see Eqs. 35 and 36)

$$\Psi_{00}^+(z) = -\lambda\sum_{\{\mathbf{k}\}}\langle 0|\delta L_N|\{\mathbf{k}\}\rangle C_{\{\mathbf{k}\}0}^+(z) \tag{A.32}$$

The authors find lastly that expression (A.25) substituted in formula (A.31) of the Prigogine theory leads to a result equivalent to the one that one obtains if one combines Eqs. (A.17–23) with the first equation of the hierarchy (6) in the Bogolubov method.

A. IV. Another Proof of the Equivalence between the Results of Cohen and of Prigogine

The demonstration, given in the main text, of the equivalence between the results of Cohen[8] and of Prigogine[14] rests on analysis

of the irreducibility condition appearing in the definition (35) for $\Psi_{00}^{+}(z)$. This study is not trivial and therefore the generalisation of our proof, although feasible in principle, is not straightforward.

Here we shall use a method that is certainly less explicit but in which this complicated analysis is not needed. Indeed, as is implicit in refs. 14 and 17, and as was noted explicitly by Weinstock[31] and George[11a] the operator $\Omega(z)$, defined by the expressions (46) and (47) also obeys the relation

$$\Omega(i0)\Psi_{00}^{+}(i0) = -z_0 \tag{A.33}$$

where z_0 is the zero of the operator equation

$$\Psi_{00}^{+}(z_0) + z_0 = 0 \tag{A.34}$$

and is itself an operator in velocity space (but this property is irrelevant for the present calculation).

Moreover, using the definition (10) of the streaming operator S_τ^N and the perturbation expansion of its Laplace transform $R_N(z)$ (see 28), it is easy to show that

$$\langle 0|S_{-\tau}^N|0\rangle = \frac{1}{2\pi i}\int_C dz\, \frac{e^{-iz\tau}}{z + \Psi_{00}^{+}(z)} \tag{A.35}$$

(for more details see refs. 16 and 19).

If we assume, as in previous works,[11a,31] that the only zero of the denominator of (A.35) that contributes to the long-time limit of this operator is z_0, we get

$$\lim_{\tau \gg \tau_c} \langle 0|S_{-\tau}^N|0\rangle = \lim_{\tau \gg \tau_c} \left[\frac{e^{-ij\tau}}{1 + \dfrac{\partial \Psi_{00}^{+}(z)}{\partial z}} \right]_{z=z_0} \tag{A.36}$$

because the other zeros are related to the finite duration of the collision.

Taking the logarithmic derivative of (A.36) with respect to τ, multiplying on both sides by $\langle 0|S_{-\tau}^N|0\rangle$, and using finally the Liouville equation (2), we have (see A.33):

$$\lim_{\tau \gg \tau_c} \lambda\langle 0|\delta L_N S_{-\tau}^N|0\rangle = -\lim_{\tau \gg \tau_c} \Omega(i0)\Psi_{00}^{+}(i0)\langle 0|S_{-\tau}^N|0\rangle \tag{A.37}$$

In this equation, the generalized Boltzmann operator $\Omega(i0)\Psi_{00}^{+}(i0)$ is now implicitly defined in terms of reducible

operators and, in the following, we shall thus be able to avoid the study of the irreducibility condition. Formula (A.37), which is equivalent to eqs. (46) and (47), together with (45), specifies completely the evolution of the N-particle distribution function.

Let us now multiply each side of (A.37) by $\prod_{j=1}^{N} \varphi_1(\mathbf{p}_j,t)$ and integrate over the dummy momenta $\mathbf{p}_2 \ldots \mathbf{p}_N$. In the limit $V \to \infty$, we may identify equal powers of V, and we then obtain

$$-i\lambda \int d\mathbf{p}_2 \ldots \int d\mathbf{p}_N \langle 0|\delta L_N S^N_{-\tau}|0\rangle^{[n]} \prod_{i=1}^{N} \varphi_1(\mathbf{p}_i,t) =$$

$$i \sum_{n'=2}^{n} N^{n'-1} \int d\mathbf{p}_2 \ldots \int d\mathbf{p}_N (\Omega(i0)\Psi^{+}_{00}(i0))^{(12\ldots n')} \langle 0|S^N_{-\tau}|0\rangle^{[n-n'+1]}$$

$$\times \prod_{i=1}^{N} \varphi_1(\mathbf{p}_i,t) \qquad \text{(A.38)}$$

where we have dropped for brevity the $\lim_{\tau \to \infty}$ and where the superscript in square braces $[n]$ indicates that we retain only the contributions of order V^{-n+1} in the corresponding operator. The quantity $(\Omega(i0)\Psi^{+}_{00}(i0))^{(12\ldots n')}$ has been defined through (85) and the origin of the factor $N^{n'-1}$ is the same as in this equation.

Let us first study separately the left-hand side of (A.38):

$$I_n = -i\lambda \int d\mathbf{p}_2 \ldots \int d\mathbf{p}_N \langle 0|\delta L_N S^N_{-\tau}|0\rangle^{[n]} \prod_{i=1}^{N} \varphi_1(\mathbf{p}_i,t) \qquad \text{(A.39)}$$

We note that the definition of δL_N (see 5) implies that the only non-vanishing contributions to I_n start with $\delta L^{(1j)}$. We specify $j = 2$ and introduce an "indistinguishability" factor $(N-1)$ (because of the $\mathbf{p}_2 \ldots \mathbf{p}_N$ integration, the particles $2, 3, \ldots, N$ play the same role). Moreover, we insert in (A.39) the dynamical cluster expansion, giving the streaming operators in terms of the $\mathcal{U}^{(n)}_{-\tau}$ operators and from which the formulae (23) have been deduced. Finally, we use the well-known results:

$$\int d\mathbf{p}_1 \ldots \int d\mathbf{p}_N \, \mathcal{U}^{(n)}_{-\tau} = 0$$

$$\langle 0|\delta L^{(12)} \mathcal{U}^{(12\ldots n)}_{-\tau}|0\rangle = O(V^{-n+1})$$

$$\langle 0|\mathcal{U}^{(12\ldots n)}_{-\tau}|0\rangle = O(V^{-n+1}) \qquad \text{(A.40)}$$

and we get (for details see ref. 4*a*):

$$I_n = -i\lambda(N-1)\frac{(N-2)!}{(N-n)!\,(n-2)!}\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n$$

$$\langle 0|\delta L^{(12)}\,\mathscr{U}^{(12\ldots n)}0\rangle \prod_{i=1}^{n}\varphi_1(\mathbf{p}_i,t) \tag{A.41}$$

In the same way, the right-hand side of (A.38) denoted $\bar{I}_n$ becomes:

$$\bar{I}_n = \sum_{n'=2}^{n} N^{n'-1}\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n (i\Omega(i0)\Psi^{+}_{00}(i0))^{(12\ldots n')}$$

$$\times \sum_{\{m_k\}} \frac{(N-n')}{(N-n'-m)!}\prod_{k=1}^{n'}\frac{\langle 0|\mathscr{U}^{(k,m_k)}_{-\tau}|0\rangle}{m_k!}\prod_{i=1}^{n}\varphi_1(\mathbf{p}_i,t) \tag{A.42}$$

where the dashed summation has the following meaning: take the $m = n - n'$ particles which do not appear in $(i\Omega(i0)\Psi^{+}_{00}(i0))^{(12\ldots n')}$ and denote them by $t_1, t_2, \ldots, t_m$; then put them in their natural order $t_1 < t_2 < \ldots < t_m$ and make all possible partitions of these particles into n' groups of m_k particles ($k = 1, 2, \ldots, n'$) such that $\sum_{k=1}^{n'} m_k = m$ (some m_k may be zero) and such that the natural order is maintained. Then, for each partition, associate the groups m_k to the corresponding particle k in the set n'; finally, form the products

$$\prod_{k=1}^{n'}\frac{\langle 0|\mathscr{U}^{(k,m_k)}_{-\tau}|0\rangle}{m_k!}\,.$$

Of course, the natural order need not be maintained and thus we have to sum over all the particle labellings. Because of the integrals over the impulsions, this gives rise simply to combinatorial factors.

Noting that $I_n = \bar{I}_n$, we may write:

$$\frac{1}{(n-2)!}\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n \langle 0|\theta_{12}\mathscr{U}^{(12\ldots n)}_{-\tau}|0\rangle \prod_{i=1}^{n}\varphi(\mathbf{p}_i,t) =$$

$$\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n\,(i\Omega(i0)\Psi^{+}_{00}(i0))^{(1\ldots n)}\prod_{i=1}^{n}\varphi_1(\mathbf{p}_i,t)$$

$$+\sum_{n'=2}^{n-1}\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n (i\Omega(i0)\Psi^{+}_{00}(i0))^{(12\ldots n')}\sum_{\{m_k\}}{}'\prod_{k=1}^{n'}\frac{\langle 0|\mathscr{U}^{(k,m_k)}_{-\tau}|0\rangle}{m_k!}$$

$$\prod_{i=1}^{n}\varphi_1(\mathbf{p}_i,t) \tag{A.43}$$

Now we shall transform the Cohen's results in order to bring them into a form equivalent to (A.43). Therefore, let us first define a new operator:*

$$B^{(n)}_{-\tau} = \frac{1}{(n-2)!}\,\theta_{12}B'^{(n)}_{-\tau} \tag{A.44}$$

where $B^{(n)}_{-\tau}$ itself is given by the equations (21) and (24). We note then that $B'^{(n)}_{-\tau}$ is the sum of all the 1,2-irreducible Husimi trees (1,2-I.H.T.) with n labelled points (see the comment following the eqs. 23 and the illustration of it given in formulae 21). On the other hand, $\mathscr{U}^{(n)}_{-\tau}$ is the sum of all the Husimi trees, whether reducible or not, with n labelled points. This is seen on the expressions (22). We may thus write:

$$\mathscr{U}^{(n)}_{-\tau} = B'^{(n)}_{-\tau} + R^{(n)}_{-\tau} \tag{A.45}$$

where $R^{(n)}_{-\tau}$ is the sum of all the 1,2-reducible Husimi trees (1,2-R.H.T.) with n labelled points.

As is easily seen on examples,[4a] each 1,2-R.H.T. with n labelled points is uniquely decomposable in a 1,2-I.H.T. with $n' < n$ labelled points plus a certain number of appending parts attached to this 1,2-chain. More precisely, the class of 1,2-R.H.T. with n labelled points is now decomposed into sub-classes, each sub-class denoted $R^{(12\ldots n)}_{(12\ldots n')}(\tau)$ being characterized by the set of n' points forming the 1,2-chain. We have then:

$$\begin{aligned} R^{(123)}_{-\tau} &= R^{(123)}_{(12)}(\tau) \\ R^{(1234)}_{-\tau} &= R^{(1234)}_{(12)}(\tau) + R^{(1234)}_{(123)}(\tau) + R^{(1234)}_{(124)}(\tau) \\ R^{(n)}_{-\tau} &= \sum_{n'=2}^{n-1} \sum_{\text{lab}} R^{(n)}_{(n')}(\tau) \end{aligned} \tag{A.46}$$

where the second sum is to be made over all labellings of the $n' - 2$ points other than 1 and 2 among the $n - 2$ points different from 1 and 2 (there are $\dfrac{(n-2)!}{(n-n')!(n'-2)!}$ such arrangements which all give the same contribution under an integral over the phases of particles 2,3 . . . n).

* In fact, this $B'^{(n)}_{-\tau}$ is exactly the operator $B^{(m)}_{-\tau}$ of ref. 4a.

Looking at examples[4a] suggests the following important remarks:

(1) The graphs of $R_{(123)}^{(1234)}(\tau)$ are made of two groups of terms: those where the 1,2-chain is $\mathscr{V}_{-\tau}^{(123)}$ and those where it is $\mathscr{V}_{-\tau}^{(13)}\, V_{-\tau}^{(23)}$. Moreover, each member of one group is in one-to-one correspondence with a member of the other when a 1,2-bound is added to, or substracted from, this element. In general, any $R_{(n')}^{(n)}(\tau)$ may be decomposed into p groups of terms (p is the number of 1,2-I.H.T. with n'-labelled points) and each member of one group is in one-to-one correspondence with an element of each other group. This means that, to get $R_{(n')}^{(n)}(\tau)$, we may add the appending parts to the sum of all the 1,2-I.H.T. with n'-labelled points, *i.e.* $B'^{(n')}_{-\tau}$, instead of adding them separately to each 1,2-I.H.T.

(2) Let us now look at the appending parts. We consider in $R_{(n')}^{(n)}(\tau)$ all the graphs where m_l labelled points are connected in one single appending part ($m_l \leqslant n - n'$) to the articulation point l of a given I.H.T. with n'-labelled points. It is easily realized that this appending part may be any of the labelled Husimi trees with $m_l + 1$ labelled points (whether reducible or not). The sum of all these graphs is thus written as the product of the operator associated with the given I.H.T. times $\mathscr{U}_{-\tau}^{(l,m_l)}$ for the appending parts.

This allows us to write:

$$R_{(12)}^{(123)}(\tau) = B'^{(12)}_{-\tau}\ [\mathscr{U}_{-\tau}^{(13)} + \mathscr{U}_{-\tau}^{(23)}]$$

$$R_{(12)}^{(1234)}(\tau) = B'^{(12)}_{-\tau}\ [\mathscr{U}_{-\tau}^{(13)}\mathscr{U}_{-\tau}^{(24)} + \mathscr{U}_{-\tau}^{(14)}\mathscr{U}_{-\tau}^{(23)} + \mathscr{U}_{-\tau}^{(134)} + \mathscr{U}_{-\tau}^{(234)}]$$

and in general, if we remember that the following result always appears under an integral over the phases:

$$R_{(n)}^{(n')}(\tau) = m!\ B'^{(12\ldots n')}_{-\tau} \sum_{\{m_k\}}{}' \prod_{k=1}^{n'} \frac{\mathscr{U}_{-\tau}^{(k,m_k)}}{m_k!} \tag{A.47}$$

where the dashed summation has the same meaning as in (A.42).

Finally, we multiply the operator equations (A.45–47) at left by θ_{12} and at right by $\prod_{i=1}^{N} \varphi_1(\mathbf{p}_i, t)$, integrate over all the phases but

that of particle 1, and go over to the wave vectors, so that we get:

$$\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n \langle 0|\theta_{12} B'^{(12\ldots n)}_{-\tau}|0\rangle \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i,t) =$$

$$\int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n \left[\langle 0|\theta_{12} \mathscr{U}^{(1\ldots n)}_{-\tau}|0\rangle \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i,t) - \right.$$

$$\left. \sum_{n'=2}^{n-1} \frac{(n-2)!}{(n'-2)!(n-n')!} \langle 0|\theta_{12} R^{(n)}_{(n')}(\tau)|0\rangle \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i,t) \right] \qquad \text{(A.48)}$$

and

$$\langle 0|\theta_{12} R^{(n)}_{(n')}(\tau)|0\rangle = m!\langle 0|\theta_{12} B'^{(12\ldots n')}_{-\tau}|0\rangle \sum'_{\{m_k\}} \prod_{k=1}^{n'} \frac{\langle 0|\mathscr{U}^{(k,m_k)}_{-\tau}|0\rangle}{m_k!} \qquad \text{(A.49)}$$

In deriving these results we had to remember the remark following (A.46) and to take into account the translational invariance of intermolecular forces. This explains why all the Fourier intermediate states in (A.48) and (A.49) have zero wave vectors.

The last two equations define $\langle 0|\theta_{12} B'^{(12\ldots n)}_{-\tau}|0\rangle$ in terms of the $\langle 0|\theta_{12} B'^{(12\ldots n')}_{-\tau}|0\rangle$ for $n > n'$. This structure is the same as that of (A.43) where $(\Omega(i0)\Psi^{+}_{00}(i0))^{(1\ldots n)}$ is given in terms of the $(\Omega(i0)\Psi^{+}_{00}(i0))^{(1\ldots n')}$. Moreover, comparing (A.43) with (A.48) and (A.49), it becomes obvious that

$$(n-2)! \int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n (i\Omega(i0)\Psi^{+}_{00}(i0))^{(1\ldots n)} \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i,t) =$$

$$\lim_{\tau\to\infty} \int d\mathbf{p}_2 \ldots \int d\mathbf{p}_n \langle 0|\theta_{12} B'^{(n)}_{-\tau}|0\rangle \prod_{i=1}^{n} \varphi_1(\mathbf{p}_i,t) \qquad \text{(A.50)}$$

Let us put this result in the generalized Boltzmann equation (92) as derived by Cohen. Remembering (A.44), we get identically the expression (85) which is the generalized Boltzmann equation in Prigogine's formalism. This completes the proof of the equivalence between the two theories.

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[Added in Proof.] We do not here discuss the logarithmic singularities which occur in the virial expansion and have recently been reported by I. Oppenheim and K. Kawasaki [*Phys. Rev.* **139A,** 1763 (1965)].

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